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The Physiology of Vision

BY

SIR C. V. RAMAN

150 Pages with six plates in half-tone and four in colour.
Published by the Indian Academy of Sciences, Bangalore-6
Price $5.00 or £2.00 or Rupees 25.00

Professor Raman's book presents in a systematic form the results of his studies of the nature of human vision and of visual processes carried out over a period of several years. They cover a wide field, indicated by the titles of its twenty-four chapters listed below. The treatise is of modest length and is written in a style which makes it easy reading. But it cuts deeply into the fundamental aspects of the subject. Professor Raman's investigations have led him to the conclusion that the trichromatic hypothesis and the duplicity theory of vision are wholly untenable and that the visual pigments which enable light to be perceived cannot be identified with the so-called visual purple found in the retina.

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CHAPTER III. The Structure and Functioning of the Retina
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MICROWAVE SPECTRUM OF PENTAFLUOROBENZENE

BY S. DORAISWAMY AND S. D. SHARMA

(*Tata Institute of Fundamental Research, Bombay* 5)

Received May 15, 1968

(Communicated by Dr. B. V. Thosar, F.A.SC.)

ABSTRACT

The microwave spectrum of pentafluorobenzene has been measured in the frequency region 12·5 to 18·00 KMHz. The spectrum is analysed on the basis of rigid asymmetric rotor theory. The rotational constants obtained are $A = 1471 \cdot 963$ MHz, $B = 1026 \cdot 278$ MHz, $C = 604 \cdot 693$ MHz and the asymmetry parameter $\kappa = -0 \cdot 0278$. The inertial defect is $\Delta = I_c - I_a - I_b = -0 \cdot 014$ amu Å². The bond distances are $d_{CF} = 1 \cdot 328$ Å and $d_{CH} = 1 \cdot 089$ Å, assuming $d_{CC} = 1 \cdot 395$ Å.

INTRODUCTION

THE present work on pentafluorobenzene is in continuation of the studies of the substituted pentafluorobenzene compounds undertaken in this laboratory. The molecule pentafluorobenzene is assumed to be planar. Using the values for d_{CC} and d_{CF} reported for pentafluorobenzonitrile[1] and hexafluorobenzene[2] and assuming $d_{CH} = 1 \cdot 084$ Å, an expected rotational spectrum

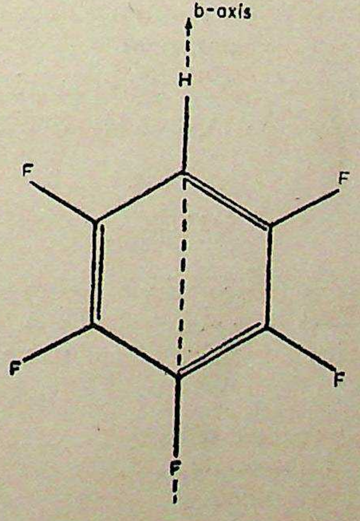

FIG. 1. Pentafluorobenzene.

was generated using computer programme written by Dr. L. Pierce.* It was found as expected that the axis of intermediate moment of inertia, along which the dipole moment lies, coincides with the C–H bond. Therefore only *b* type transitions are permitted with the selection rules $\triangle K_{-1} = \pm 1$ and $\triangle K_1 = \pm 1$. Pentafluorobenzene has a rich spectrum. There are lines every 5 to 10 MHz in K band region (18–26 GHz) and as such the investigation was undertaken in the KU band (12·5–18 GHz) even where there are numerous lines. The spectrum showed strong Q lines of high J but R lines were comparatively weak and could not be resolved by Stark effect. So Stark effect was of no help in the assignment of the spectrum. The analysis was therefore carried out by the identification of Q lines as starting point and later completing it by finding R lines.

EXPERIMENTAL

A conventional 100 KHz Stark modulated microwave spectrometer was used for the investigation of this molecule. The compound pentafluorobenzene was obtained from Imperial Smelting Corporation and was used without further purification. The measurements were all made at dry ice temperature and the pressure in most of the cases was maintained below 10 microns. As reported in the earlier paper,[1] the frequency measurements were made by comparing the Klystron frequency with the harmonics of a James Knights JKTO-43 10–MHz crystal Oscillator. Frequencies of the lines were determined by superimposing a frequency marker directly upon the absorption maxima on the oscilloscope. The frequencies of the absorption lines were determined by sweeping both from lower to higher frequencies and from higher to lower frequencies. The values obtained are the averages of these two values; the reproducibility is within a MHz in most cases. The observed spectra consisted of many lines which are narrower than those of pentafluorobenzonitrile. Excepting a few which were insensitive, the lines exhibited quadratic Stark effect—both regular and inverted.

ANALYSIS

Assuming a regular hexagonal structure for the carbon ring and with $d_{CC} = 1{\cdot}394$ Å, $d_{CF} = 1{\cdot}328$ Å and $d_{CH} = 1{\cdot}084$ Å, the spectrum was generated. The programme written by Dr. Pierce was used with slight alterations to suit the CDC 3600 computer. The rotational constants used were A = 1472·916 MHz, B = 1026·906 MHz and C = 605·062 MHz. Comparing the observed and calculated spectra, an attempt was made initially to assign a few R lines. The frequency of an R branch line can be written as[3]

---

* This programme was kindly provided to us by Dr. C. Thomas of Harvard University, 12 Oxford Street, Cambridge 38, Massachusetts, U.S.A.

$$\nu = \left(\frac{A+C}{2}\right) 2J'' + \left(\frac{A-C}{2}\right) \Delta E\ (\kappa) \tag{1}$$

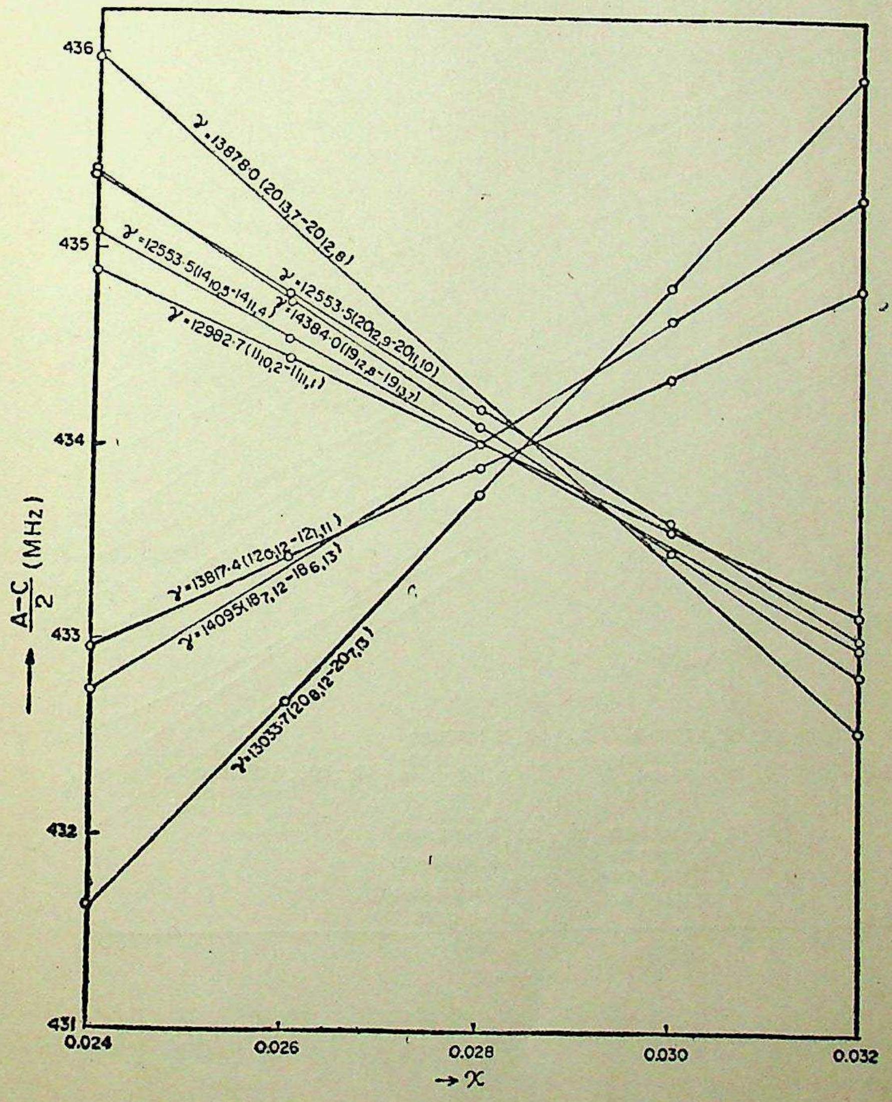

FIG. 2. Initial plot of (A−C)/2 *vs.* κ for pentafluorobenzene assigning the observed frequencies to the nearest calculated frequencies of transitions.

where $\triangle E = E''(\kappa) - E'(\kappa)$. J″ and E″ refer to the higher level and E′ to the lower. The values of $(A + C)/2$ and $(A - C)/2$ obtained from such an assignment for $\kappa = -0{\cdot}028$ were 1038·93 MHz and 433·91 MHz respectively. But the Q lines predicted by this $(A - C)/2$ and the values of κ around $-0{\cdot}028$ did not give a satisfactory agreement.

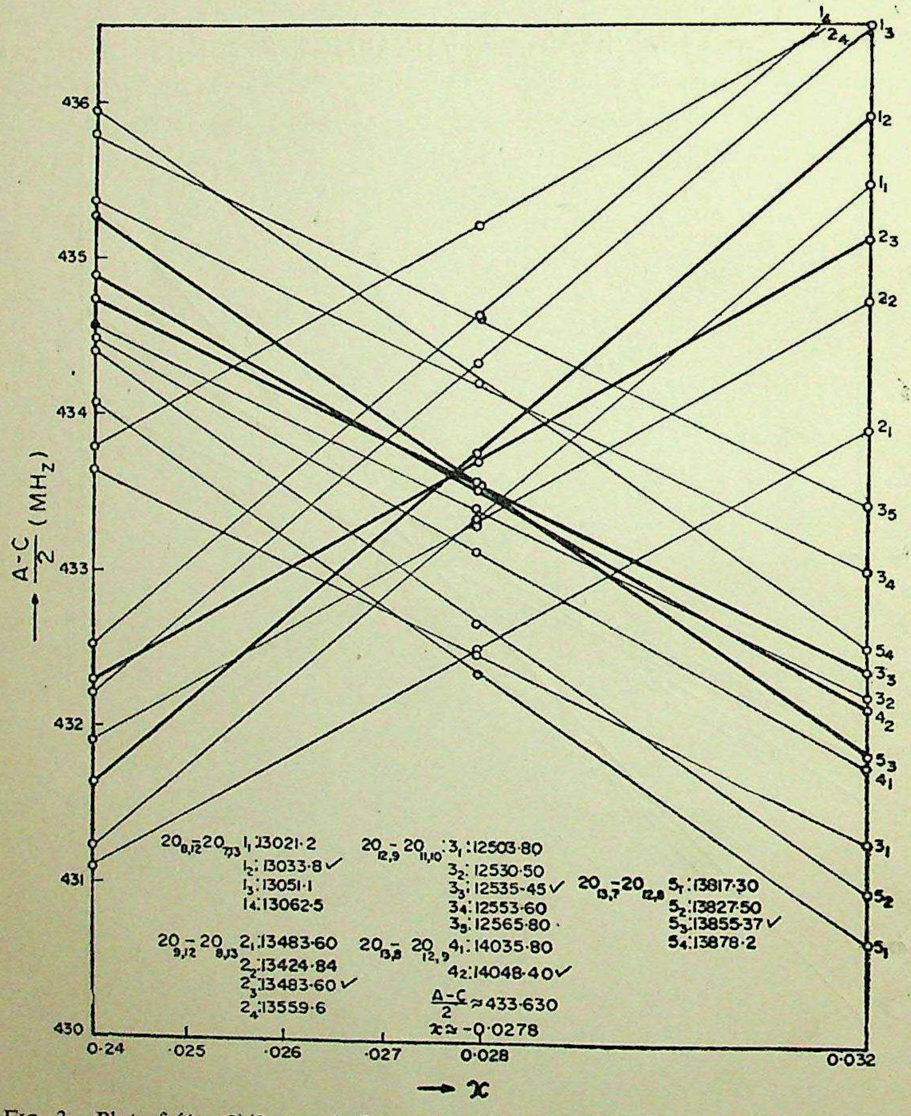

FIG. 3. Plot of $(A-C)/2$ *vs.* κ for pentafluorobenzene for a few of the transitions of $J = 20$ series assigning a number of observed frequencies around a calculated frequency of a transition to the same transition.

For Q lines $\triangle J = 0$ and therefore $\nu = (A - C)/2 \triangle E(\kappa)$. It was decided to plot for a few observed transitions the value of $(A - C)/2$ calculated as a function of κ.[4] The lines correctly assigned should all intersect at the correct values of these two parameters. For each calculated transition the nearest and most probable observed frequency was assigned and a number of plots were made. One of them is shown in Fig. 2. It is clear from the plot that no conclusion is possible. The reason was that the observed lines were so numerous that the correct assignment was not always possible. Therefore the Q line plot was tried for a few strong transitions of the J = 20 series alone. For each transition all the observed frequencies lying about

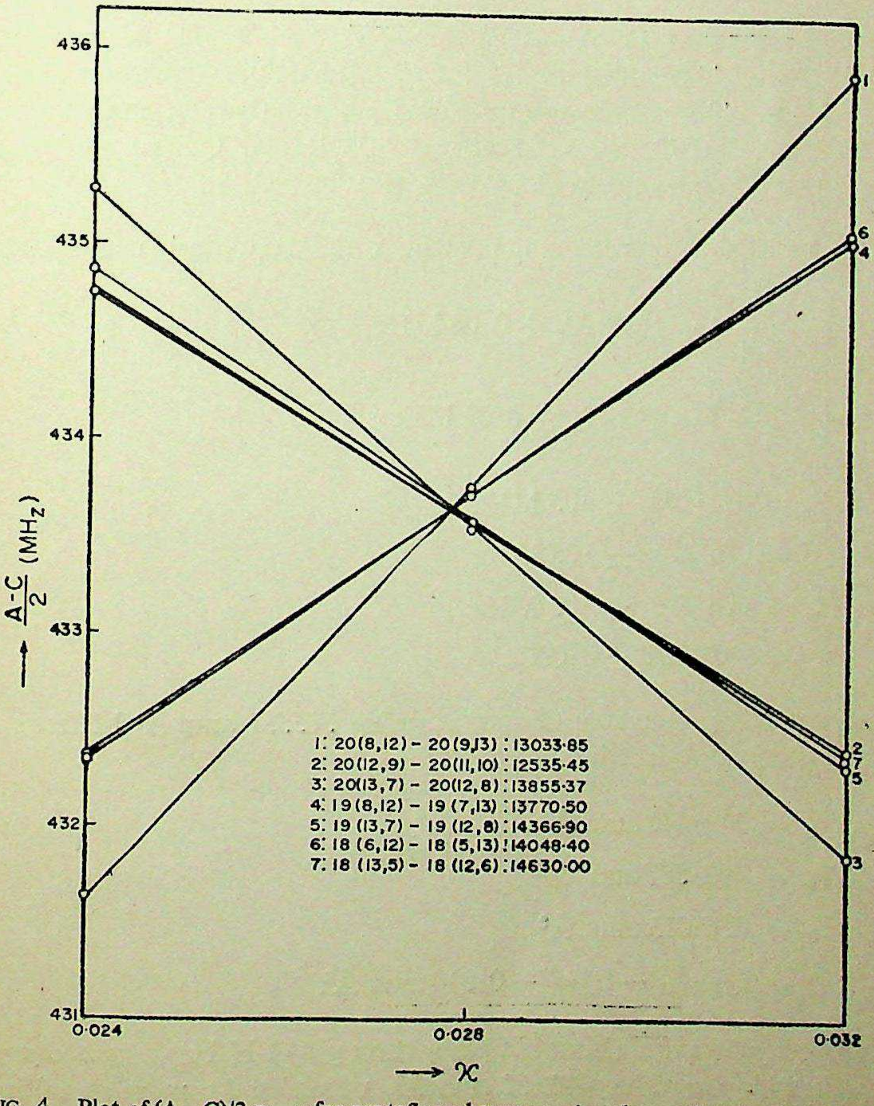

FIG. 4. Plot of $(A-C)/2$ *vs.* κ for pentafluorobenzene using the predicted values of $(A-C)/2$ and κ from Fig. 3. The intersection of these lines gave the final value of $(A-C)/2$ and κ.

50 MHz above and below the calculated frequency were assigned to the same transition. This gave a series of parallel lines for each transition. The result is shown in Fig. 3. The region of intersection of the thick lines seems to give a consistent solution for the transitions in question. To check the validity of the result in Fig. 3, Q branch lines of the series of $J = 19, 18, 17$, etc., were generated from these values of $(A - C)/2$ and κ and a new Q line plot was drawn incorporating the lines from other transitions. As can be seen in Fig. 4, all the lines intersect around $\kappa = -0{\cdot}0278$ and the corresponding $(A - C/2)$ value is 433·63 MHz.

With these values of $(A - C)/2$ and κ, $(A + C)/2$ was calculated using a few R lines. The value of $(A + C)/2$ thus obtained came out to be 1038·33 MHz. The whole spectrum was generated using these values of $(A + C)/2$, $(A - C)/2$ and κ. Some of the R and Q lines are listed in Tables I and II respectively along with the observed values.

The molecular constants consistent with these assignments are

$$\left(\frac{A+C}{2}\right) = 1038{\cdot}32_8 \pm 0{\cdot}04 \text{ MHz}$$

$$\left(\frac{A-C}{2}\right) = 433{\cdot}62_5 \pm 0{\cdot}02 \text{ MHz}$$

$$A = 1471{\cdot}963 \pm {\cdot}05 \text{ MHz}$$

$$B = 1026{\cdot}278 \pm {\cdot}05 \text{ MHz}$$

$$C = 604{\cdot}693 \pm {\cdot}05 \text{ MHz}$$

$$\kappa = -0{\cdot}0278 \pm 0{\cdot}0001.$$

The corresponding moments of inertia (using 505531 amu Å² MHz as conversion factor) and inertial defect are

$$I_a = 343{\cdot}440 \text{ amu Å}^2$$

$$I_b = 492{\cdot}587 \text{ amu Å}^2$$

$$I_c = 836{\cdot}013 \text{ amu Å}^2$$

$$\Delta = I_c - I_a - I_b = -0{\cdot}014 \text{ amu Å}^2.$$

The moment of inertia about the axis through C–H bond here compares fairly well with the value 492·32 amu Å², which is the moment of inertia about the axis through the $C - C \equiv N$ bond for pentafluorobenzonitrile,[1]

TABLE I

R branch transitions

Transition	$\nu_{\text{cal.}}$ (MHz)	$\nu_{\text{obs.}}$ (MHz)
5 (5, 1)– 4 (4, 0)	14086·7	14086·8
6 (6, 1)– 5 (5, 0)	17038·7	17038·3
6 (6, 0)– 5 (5, 1)	17043·1	17042·8
7 (5, 3)– 6 (4, 2)	17090·6	17090·6
8 (3, 6)– 7 (2, 5)	12922·8	12922·6
9 (1, 8)– 8 (2, 7)	12700·9	12700·2
9 (2, 7)– 8 (3, 6)	13877·3	13877·6
10 (0, 10)– 9 (1, 9)	12698·8	12698·1
10 (1, 10)– 9 (0, 9)		
10 (2, 9)– 9 (1, 8)	13912·0	13912·4
10 (2, 8)– 9 (3, 7)	15119·2	11518·4
10 (3, 8)– 9 (2, 7)	15155·6	15155·2
10 (3, 7)– 9 (4, 6)	16152·2	16151·6
10 (4, 7)– 9 (3, 6)	16671·1	16670·4
10 (4, 6)– 9 (5, 5)	16025·1	16025·0
11 (0, 11)–10 (1, 10)	13908·2	13908·1
11 (1, 11)–10 (0, 10)		
11 (1, 10)–10 (2, 9)	15119·2	15118·4
11 (2, 10)–10 (1, 9)	15120·1	
11 (2, 9)–10 (3, 8)	16336·1	16335·6
11 (3, 9)–10 (2, 8)	16346·3	16347·1
11 (3, 8)–10 (4, 7)	17503·1	17503·6
12 (0, 12)–11 (1, 11)	15117·5	15118·4
12 (1, 12)–11 (0, 11)		
13 (0, 13)–12 (1, 12)	16326·8	16324·7
13 (1, 13)–12 (0, 12)		

TABLE II

Q-branch transitions

Transition	$\nu_{\text{cal.}}$ (MHz)	$\nu_{\text{obs.}}$ (MHz)
11 (1, 10)–11 (0, 11)	12599·6	12599·1
11 (2, 10)–11 (1, 11)		
12 (1, 11)–12 (0, 12)	13811·0	13810·8
12 (2, 11)–12 (1, 12)		
13 (1, 12)–13 (0, 13)	15021·9	15021·8
13 (2, 12)–13 (1, 13)		
14 (1, 13)–14 (0, 14)	16232·6	16231·9
14 (2, 13)–14 (1, 14)		
14 (11, 3)–14 (10, 4)	12531·0	12530·5
15 (1, 14)–15 (0, 15)	17443·0	17441·9
15 (2, 14)–15 (1, 15)		
15 (3, 12)–15 (2, 13)	14760·2	14760·0
15 (4, 12)–15 (3, 13)	14760·5	
15 (12, 4)–15 (11, 5)	13810·2	13810·8
16 (6, 11)–16 (5, 12)	13106·1	13105·7
16 (12, 5)–16 (11, 6)	13602·0	13602·1
17 (5, 12)–17 (4, 13)	14347·3	14348·2
17 (6, 12)–17 (5, 13)	14355·8	14356·0
17 (7, 11)–17 (6, 12)	12823·4	12823·6
17 (14, 4)–17 (13, 5)	16337·3	16338·1
17 (14, 3)–17 (13, 4)	16337·1	
18 (6, 12)–18 (5, 13)	14048·6	14048·4

TABLE II (*Contd.*)

Transition	$\nu_{\text{cal.}}$ (MHz)	$\nu_{\text{obs.}}$ (MHz)
18 (12, 7)–18 (11, 8)	13062·7	13062·5
18 (13, 6)–18 (12, 7)	14646·6	14646·6
18 (13, 5)–18 (12, 6)	14630·6	14630·0
19 (8, 12)–19 (7, 13)	13770·4	13770·5
19 (12, 8)–19 (11, 9)	12769·8	12768·5
19 (13, 7)–19 (12, 8)	14366·3	14366·9
19 (13, 6)–19 (12, 7)	14306·3	14305·8
20 (7, 13)–20 (6, 14)	14999·4	14998·4
20 (8, 12)–20 (7, 13)	13033·7	13033·9
20 (9, 12)–20 (8, 13)	13437·1	13437·2
20 (12, 9)–20 (11, 10)	12535·4	12535·5
20 (13, 8)–20 (12, 9)	14049·9	14049·5
20 (13, 7)–20 (12, 8)	13855·2	13855·4
21 (8, 13)–21 (7, 14)	14541·8	14541·5
21 (9, 13)–21 (8, 14)	14700·7	14701·8
21 (14, 8)–21 (13, 9)	15368·7	15367·4
22 (14, 9)–22 (13, 10)	15024·6	15023·8
22 (14, 8)–22 (13, 9)	14809·4	14809·9
23 (9, 14)–23 (8, 15)	15427·0	15427·9
23 (15, 9)–23 (14, 10)	16358·9	16360·1
23 (15, 8)–23 (14, 9)	16281·3	16279·5
24 (14, 10)–24 (13, 11)	13023·2	13021·2
24 (15, 9)–24 (14, 10)	15753·1	15751·8

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TABLE II (*Contd.*)

Transition	$\nu_{\text{cal.}}$ (MHz)	$\nu_{\text{obs.}}$ (MHz)
25 (15, 11)–25 (14, 12)	15613·8	15613·5
26 (12, 15)–26 (11, 16)	16105·8	16106·5
26 (15, 12)–26 (14, 13)	15301·6	15302·5
27 (13, 15)–27 (12, 16)	15756·4	15756·9
27 (14, 14)–27 (13, 15)	14812·7	14811·8
28 (15, 14)–28 (14, 15)	15243·9	15244·6
28 (16, 13)–28 (15, 14)	16204·8	16205·3
29 (15, 15)–29 (14, 16)	15663·3	15663·2
29 (16, 13)–29 (15, 14)	13159·7	13160·8
30 (16, 15)–30 (15, 16)	16102·8	16102·7
31 (17, 14)–31 (16, 15)	13927·3	13926·7
32 (15, 17)–32 (14, 18)	13982·3	13981·3
33 (17, 17)–33 (16, 18)	17340·4	17340·5
34 (16, 18)–34 (15, 19)	14582·2	14582·2
35 (17, 18)–35 (16, 19)	12867·6	12869·6
36 (19, 17)–36 (18, 18)	13676·3	13677·7
38 (19, 19)–38 (18, 20)	12563·9	12565·8
40 (20, 20)–40 (19, 21)	13117·6	13118·2
40 (21, 19)–40 (20, 20)	15058·1	15058·7
41 (20, 21)–41 (19, 22)	14489·8	14489·0
42 (22, 20)–42 (21, 21)	15751·5	15751·5
43 (22, 21)–43 (21, 22)	14354·3	14352·8
45 (23, 22)–45 (22, 23)	14968·0	14965·0
47 (23, 24)–47, (22, 25)	16066·0	16062·7
50 (25, 25)–50 (24, 26)	15860·9	15864·6

The moment of inertia I_b through the CH bond is given by

$$I_b = 3\,[M_C d_{CC}^2 + M_F\,(d_{CC} + d_{CF})^2] \tag{3}$$

where M_C and M_F are the masses of carbon and fluorine atoms respectively. Assuming d_{CC} to be 1·395 Å d_{CF} comes out to be 1·328 Å which is in good agreement with the values reported earlier.[1,2]

The value obtained for I_a[3] was used to calculate the bond length d_{CH}

$$I_a = I_b - M_F\,(d_{CC} + d_{CF})^2 + M_H\,(d_{CC} + d_{CH})^2 - \frac{[M_H\,(d_{CC} + d_{CH}) - M_F\,(d_{CC} + d_{CF})]^2}{M} \tag{4}$$

where M is the total molecular weight. The value of d_{CH} from this calculation is 1·089 Å which is about 0·005 Å higher than the value of d_{CH} in benzene obtained by Stoicheff.[5]

DISCUSSION

Assuming $d_{CC} = 1\cdot394$ Å, d_{CF} was found from I_b to be 1·329 Å. Using these two values, d_{CH} was calculated from I_a as 1·098 Å. This value of $d_{CH} = 1\cdot098$ Å appears to be high since d_{CH} cannot be expected to change this much from the reported value of $d_{CH} = 1\cdot084$ Å for benzene.[5] On the other hand assuming $d_{CC} = 1\cdot396$ Å, d_{CF} comes out to be 1·326 Å and $d_{CH} = 1068$ Å. This value of d_{CH} is rather low. It is clear that a slight change in d_{CC} drastically affects d_{CH} value.

Therefore for the value of d_{CH} around 1·084 Å, d_{CC} is assumed to be 1·395 Å which leads to $d_{CF} = 1\cdot328$ Å.

At the time of completion of the present work, Sørensen *et al.*[6] reported that the d_{CF} value reported by Rachman is high and it should be 1·318 Å for 1, 2 fluorobenzene and 1·308 Å for 1, 3 fluorobenzene. Our efforts to fit the spectra with the above values of d_{CF} were not successful. We therefore consider that the value of d_{CF} in pentafluorobenzene compounds is of the order of 1·328 Å.

ACKNOWLEDGEMENTS

We wish to sincerely thank Prof. B. Venkataraman for his encouragement and advice throughout this work. We are grateful to Prof. B. N. Bhattacharya for many helpful discussions and useful comments. Our sincere thanks are due to Dr. C. Thomas, for providing us with the Computer programme of Dr. L. Pierce and Shri Prabhananda for the pains he took to make the computer programme work.

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INFORMATION OF ORDER α AND TYPE β

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Abstract

Information $I_\alpha^\beta(Q/P)$ of order α and type β is introduced and it is shown that for every fixed β, this information is a monotonic increasing function of α. It is also shown that information of order α and type 1 is non-negative when $\sum_{k=1}^{N} q_k \geqslant \sum_{k=1}^{N} p_k$, where $(q_1, q_2, \ldots, q_N)$ and $(p_1, p_2, \ldots, p_N)$ are generalised probability distributions for Q and P respectively.

1. Introduction

Let P denote the original unconditional distribution of a random variable ξ and let Q denote the conditional distribution of ξ under the condition that an event E, connected in some way with ξ, has taken place. The measure of the amount of information concerning the random variable contained in this observation is denoted by $I(Q/P)$. If

$$P(\xi = x_k) = p_k;\; P(\xi = x_k \mid E) = q_k;\; (k = 1, 2, \ldots, N) \tag{1}$$

then a possible measure of the amount of information in question is

$$I_1\left(\frac{Q}{P}\right) = \sum_{k=1}^{N} q_k \log_2 \frac{q_k}{p_k}. \tag{2}$$

Renyi[1] considered the problem of finding a suitable measure for generalised probability distributions for which

$$\sum_{k=1}^{N} p_k \leqslant 1;\quad \sum_{k=1}^{N} q_k \leqslant 1 \tag{3}$$

and obtained a more general measure for $I(Q/P)$, *viz.*,

$$I_\alpha\left(\frac{Q}{P}\right) = \frac{1}{\alpha - 1} \log_2 \frac{\sum_{k=1}^{N} \frac{q_k^{\alpha}}{p_k^{\alpha-1}}}{\sum_{k-1}^{N} q_k},\; (\alpha \neq 1). \tag{4}$$

When $\alpha \to 1$, we get as a limit

$$I_1\left(\frac{Q}{P}\right) = \frac{\sum_{k=1}^{N} q_k \log_2 \frac{q_k}{p_k}}{\sum_{k=1}^{N} q_k}. \tag{5}$$

For a complete distribution, (5) reduces to (2). $I_\alpha(Q/P)$ may be called the information of order α when the distribution P is replaced by the distribution Q.

In the present paper we shall study some of the properties of $I_\alpha(Q/P)$ and also extend these to the more general case of information of order α and type β. Renyi's information comes out to be a particular case of this when $\beta = 1$.

2. RENYI'S POSTULATES FOR INFORMATION OF ORDER α

(i) $I(Q/P)$ is unchanged if the elements of P and Q are arranged in the same way so that the one-to-one correspondence between them is unchanged.

(ii) If $P = (p_1, p_2, \ldots, p_N)$ and $Q = (q_1, q_2, \ldots, q_N)$ and $p_k \leqslant q_k$ for $k = 1, 2, \ldots, N$, then $I(Q/P) \geqslant 0$, while if $p_k \geqslant q_k$ for all k, then $I(Q/P) \leqslant 0$.

(iii) $I(\{1\} \mid \{2\}) = 1.$ (6)

(iv) If $I(Q_1/P_1)$ and $I(Q_2/P_2)$ are defined and $P = P_1 * P_2$, $Q = Q_1 * Q_2$ and the correspondences between the elements of P and Q is that induced by the correspondence between the elements of P_1 and Q_1 and those of P_2 and Q_2, then

$$I\left(\frac{Q}{P}\right) = I\left(\frac{Q_1}{P_1}\right) + I\left(\frac{Q_2}{P_2}\right). \tag{7}$$

(v) There exists a continuous and strictly increasing function $y = g(x)$ defined for all real x, such that if $I(Q_1/P_1)$ and $I(Q_2/P_2)$ are defined and

$$0 < W(P_1) + W(P_2) \leqslant 1 \quad \text{and} \quad 0 < W(Q_1) + W(Q_2) \leqslant 1, \tag{8}$$

and the correspondence between the elements of $P_1 U P_2$, $Q_1 U Q_2$ is that induced between the elements of P_1 and Q_1 and between those of P_2 and Q_2, then we have

$$g\left[\mathrm{I}\left\{\frac{(\mathrm{Q}_1\mathrm{U}\mathrm{Q}_2)}{(\mathrm{P}_1\mathrm{U}\mathrm{P}_2)}\right\}\right]$$

$$=\frac{\mathrm{W}(\mathrm{Q}_1)\, g\left[\mathrm{I}\left(\frac{\mathrm{Q}_1}{\mathrm{P}_1}\right)\right]+\mathrm{W}(\mathrm{Q}_2)\, g\left[\mathrm{I}\left(\frac{\mathrm{Q}_2}{\mathrm{P}_2}\right)\right]}{\mathrm{W}(\mathrm{Q}_1)+\mathrm{W}(\mathrm{Q}_2)}. \tag{9}$$

Under these postulates Renyi showed that $g(x)$ is either a linear or an exponential function and these functions give rise to (5) and (4) respectively.

3. Our Postulates for Information of Order α and Type β

The first four postulates are the same as those of Renyi. In the fifth postulate, the weights are replaced by

$$\mathrm{W}_\beta(\mathrm{P})=p_1{}^\beta+p_2{}^\beta+\ldots+p_\mathrm{N}{}^\beta;\ \mathrm{W}_\beta(\mathrm{Q})=q_1{}^\beta+q_2{}^\beta+\ldots+q_\mathrm{N}{}^\beta, \tag{10}$$

so that (8) and (9) are replaced respectively by

$$0<\mathrm{W}_\beta(\mathrm{P}_1)+\mathrm{W}_\beta(\mathrm{P}_2)\leqslant 1 \quad \text{and} \quad 0<\mathrm{W}_\beta(\mathrm{Q}_1)+\mathrm{W}_\beta(\mathrm{Q}_2)\leqslant 1 \tag{11}$$

and

$$g\,[\mathrm{I}\,\{(\mathrm{Q}_1\mathrm{U}\mathrm{Q}_2)\,|\,(\mathrm{P}_1\mathrm{U}\mathrm{P}_2)\}]$$

$$=\frac{\mathrm{W}_\beta(\mathrm{Q}_1)\, g\left[\mathrm{I}\left(\frac{\mathrm{Q}_1}{\mathrm{P}_1}\right)\right]+\mathrm{W}_\beta(\mathrm{Q}_2)\, g\left[\mathrm{I}\left(\frac{\mathrm{Q}_2}{\mathrm{P}_2}\right)\right]}{\mathrm{W}_\beta(\mathrm{Q}_1)+\mathrm{W}_\beta(\mathrm{Q}_2)}. \tag{12}$$

The advantage of using $\mathrm{W}_\beta(\mathrm{P})$ instead of $\mathrm{W}(\mathrm{P})$ has been explained earlier.[2]

With this modification, and proceeding in the same way as Renyi,[1] we get

$$\mathrm{I}_\alpha{}^\beta\left(\frac{\mathrm{Q}}{\mathrm{P}}\right)=\frac{1}{\alpha-1}\log_2\frac{\sum\limits_{k=1}^{\mathrm{N}} q_k{}^\beta\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum\limits_{k=1}^{\mathrm{N}} q_k{}^\beta};\quad (\alpha=1) \tag{13}$$

and

$$\mathrm{I}_1{}^\beta\left(\frac{\mathrm{Q}}{\mathrm{P}}\right)=\frac{\sum\limits_{k=1}^{\mathrm{N}} q_k{}^\beta\log_2\frac{q_k}{p_k}}{\sum\limits_{k=1}^{\mathrm{N}} q_k{}^\beta}. \tag{14}$$

When $\beta = 1$, these reduce to Renyi's measure of information of order α and 1 respectively. Postulates (i), (ii), (iii) are easily verified. For verifying (iv), we have

$$I_\alpha^\beta\left(\frac{Q}{P}\right) = \frac{1}{\alpha - 1}\log_2 \frac{\sum_{k=1}^{N}\sum_{j=1}^{M}(q_k^2)^\beta (q_j')^\beta \left(\frac{q_k^2}{p_k^2}\frac{q_j'}{p_j'}\right)^{\alpha-1}}{\sum_{k=1}^{N}\sum_{j=1}^{M}(q_k^2)^\beta (q_j')^\beta}$$

$$= \frac{1}{\alpha - 1}\log_2 \frac{\sum_{k=1}^{N}(q_k^2)^\beta \left(\frac{q_k^2}{p_k^2}\right)^{\alpha-1} \sum_{j=1}^{M}(q_j')^\beta \left(\frac{q_j'}{p_j'}\right)^{\alpha-1}}{\sum_{k=1}^{N}(q_k^2)^\beta \sum_{j=1}^{M}(q_j')^\beta}$$

$$= I_\alpha^\beta\left(\frac{Q_2}{P_2}\right) + I_\alpha^\beta\left(\frac{Q_1}{P_1}\right). \tag{15}$$

Similarly it is verified that (12) will be satisfied. The postulates are also easy to verify in the limit when $\alpha \to 1$.

4. NON-NEGATIVE CHARACTER OF $I_\alpha(Q/P)$ WHEN $\alpha > 1$

According to postulate (ii), $I_\alpha(Q/P)$ can be both positive and negative. We show however that if

$$\sum_{k=1}^{N} p_k \leq \sum_{k=1}^{N} q_k \tag{16}$$

then

$$I_\alpha\left(\frac{Q}{P}\right) \geqslant 0. \tag{17}$$

This includes the case when P and Q are complete probability distributions.

We use Jensen's theorem which states[3]:

"Let $a_1, a_2, \ldots, a_N$ be arbitrary positive numbers, then if $\phi''(t)$ exists and $\phi(t)$ is convex in $\alpha \leqslant t \leqslant \beta$, then

$$\phi\left(\frac{a_1 t_1 + a_2 t_2 + \ldots + a_N t_N}{a_1 + a_2 + \ldots + a_N}\right) \leqslant \frac{a_1\phi(t_1) + \ldots + a_N\phi(t_N)}{a_1 + a_2 + \ldots + a_N}. \tag{18}$$

Further if $\phi(t)$ is continuous and convex, sign of equality can hold only if all t's are equal or $\phi(t)$ is linear.

The inequality is reversed if the function $\phi(t)$ is concave." We apply the theorem to the function

$$\phi(t) = \log x^{\alpha-1} \tag{19}$$

which is convex if $\alpha < 1$ and concave if $\alpha > 1$.

Case (*i*).—If $\alpha > 1$, this gives

$$\frac{\sum_{k=1}^{N} q_k \log \left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N} q_k} \leqslant \log \left(\frac{\sum_{k=1}^{N} q_k \left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N} q_k} \right)^{\alpha-1}$$

or

$$(\alpha - 1) \frac{\sum_{k=1}^{N} q_k \log \frac{q_k}{p_k}}{\sum_{k=1}^{N} q_k} \leqslant (\alpha - 1) \frac{\sum_{k=1}^{N} q_k \left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N} q_k} \tag{20}$$

or

$$I_\alpha \left(\frac{Q}{P}\right) \geqslant \frac{1}{\alpha - 1} \frac{\sum_{k=1}^{N} q_k \log \frac{q_k}{p_k}}{\sum_{k=1}^{N} q_k}. \tag{21}$$

Again from the same theorem (since $\log x$ is concave),

$$\frac{\sum_{k=1}^{N} q_k \log \frac{p_k}{q_k}}{\sum_{k=1}^{N} q_k} \leqslant \log \left(\frac{\sum_{k=1}^{N} q_k \frac{p_k}{q_k}}{\sum_{k=1}^{N} q_k} \right) = \log \frac{\sum_{k=1}^{N} p_k}{\sum_{k=1}^{N} q_k} \leqslant 0, \tag{22}$$

since we are assuming

$$\sum_{k=1}^{N} p_k \leqslant \sum_{k=1}^{N} q_k.$$

From (21) and (22)

$$I_\alpha \left(\frac{Q}{P}\right) \geqslant 0 \text{ when } \alpha > 1. \tag{23}$$

The inequality sign holds when all q_k/p_k are equal. In this case $I_\alpha(Q/P) = 0$, *i.e.*, no information is obtained by the observation of E.

Case (*ii*).—The proof for $\alpha \leqslant 1$ will be given in the next section.

5. MONOTONIC CHARACTER OF I_α (Q/P)

$$\frac{d}{d\alpha}\left[I_\alpha\left(\frac{Q}{P}\right)\right]=\frac{d}{d\alpha}\left[\frac{1}{\alpha-1}\log\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}\right]$$

$$=\frac{1}{\alpha-1}\,\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}\log\left(\frac{q_k}{p_k}\right)}{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}-\frac{1}{(\alpha-1)^2}\log\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}$$

$$=\frac{1}{(\alpha-1)^2}\left\{\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}\log\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}\left(\frac{q_k}{p_k}\right)^{\alpha-1}}-\log\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}\right\}. \tag{24}$$

Applying Jensen's theorem to the convex function $x \log x$ and putting

$$a_k=q_k,\quad t_k=\left(\frac{q_k}{p_k}\right)^{\alpha-1},$$

we get

$$\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}\log\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}\le\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}\log\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}$$

or

$$\log\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k}\leqslant\frac{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}\log\left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N}q_k\left(\frac{q_k}{p_k}\right)^{\alpha-1}}. \tag{25}$$

Thus

$$\frac{d}{d\alpha}\left[I_\alpha\left(\frac{Q}{P}\right)\right]\geqslant 0,$$

so that I_α(Q/P) is a monotonic increasing function of α for all α. Now

$$I_0\left(\frac{Q}{P}\right)=-\log_2\frac{\sum_{k=1}^{N}q_k\left(\frac{p_k}{q_k}\right)}{\sum_{k=1}^{N}q_k}$$

$$= -\log_2 \frac{\sum_{k=1}^{N} p_k}{\sum_{k=1}^{N} q_k} = \log_2 \frac{\sum_{k=1}^{N} q_k}{\sum_{k=1}^{N} p_k}. \tag{26}$$

If

$$\sum_{k=1}^{N} p_k \leqslant \sum_{k=1}^{N} q_k, \tag{27}$$

$$I_0\left(\frac{Q}{P}\right) \geqslant 0. \tag{28}$$

Since $I_\alpha(Q/P)$ is a monotonic increasing function of α, $I_\alpha(Q/P) \geqslant 0$ for all α. This completes the proof of the result of the last section for $\alpha \leqslant 1$.

6. THE CASE WHEN $\sum_{k=1}^{N} p_k \neq \sum_{k=1}^{N} q_k$

It is obvious from (26) that if

$$\sum_{k=1}^{N} q_k > \sum_{k=1}^{N} p_k,$$

then $I_0(Q/P) > 0$ and as such the non-negative character of $I_\alpha(Q/P)$ is maintained for all α whenever

$$\sum_{k=1}^{N} q_k \geqslant \sum_{k=1}^{N} p_k.$$

If

$$\sum_{k=1}^{N} q_k < \sum_{k=1}^{N} p_k,$$

then $I_0(Q/P)$ is negative and there will be a range of values of α for which $I_\alpha(Q/P)$ will be negative.

To examine whether it will be positive somewhere, we consider the variation as $\alpha \to \infty$.

Since

$$\sum_{k=1}^{N} q_k < \sum_{k=1}^{N} p_k,$$

two possibilities arise.

(i) $q_k < p_k$ for all k. In this case

$$I_1\left(\frac{Q}{P}\right) = \frac{\sum_{k=1}^{N} q_k \log\left(\frac{q_k}{p_k}\right)}{\sum_{k=1}^{N} q_k}. \tag{29}$$

Since $q_k < p_k$ for all k, $\log q_k/p_k < 0$ for all k and as such

$$I_1\left(\frac{Q}{P}\right) < 0. \tag{30}$$

For $\alpha > 1$,

$$\left(\frac{q_k}{p_k}\right) < 1 \text{ implies} \left(\frac{q_k}{p_k}\right)^{\alpha-1} < 1$$

so that

$$\sum_{k=1}^{N} q_k \left(\frac{q_k}{p_k}\right)^{\alpha-1} < \sum_{k=1}^{N} q_k$$

and

$$\frac{1}{\alpha-1} \log_2 \frac{\sum_{k=1}^{N} q_k \left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N} q_k} < 0. \tag{31}$$

Thus $I_\alpha(Q/P)$ is negative for all α. This is of course one of the postulates for Renyi's information of order α.

(ii) $\sum_{k=1}^{N} q_k < \sum_{k=1}^{N} p_k$,

but at least for one k, $q_k > p_k$.

Let q_M/p_M be the largest of $\{q_k/p_k\}$, and let q_M be the largest of $\{q_k\}$,

$$\underset{\alpha\to\infty}{Lt} \frac{1}{\alpha-1} \log \frac{\sum_{k=1}^{N} q_k \left(\frac{q_k}{p_k}\right)^{\alpha-1}}{\sum_{k=1}^{N} q_k}$$

$$= \underset{\alpha \to \infty}{\mathrm{L}t} \frac{1}{\alpha - 1} \log \frac{q_{\mathrm{M}} \left(\frac{q_{\mathrm{M}}}{p_{\mathrm{M}}}\right)^{\alpha-1}}{q_{\mathrm{M}}}$$

$$= \log \left(\frac{q_{\mathrm{M}}}{p_{\mathrm{M}}}\right). \tag{32}$$

Since $q_{\mathrm{M}}/p_{\mathrm{M}} > 1$, $\mathrm{I}_{\infty}(\mathrm{Q/P}) > 0$ and as such $\mathrm{I}_{\alpha}(\mathrm{Q/P}) > 0$ for some value of α, but if q_{M} is not the largest, even $\mathrm{I}_{\infty}(\mathrm{Q/P})$ may be negative.

We can see the result in another way.

Let

$$\sum_{k=1}^{\mathrm{N}} q_k = \mathrm{A}, \quad \sum_{k=1}^{\mathrm{N}} p_k = \mathrm{B}$$

$$q_k' = \frac{q_k}{\mathrm{A}}, \quad p_k' = \frac{p_k}{\mathrm{B}},$$

so that

$$\sum_{k=1}^{\mathrm{N}} q_k' = 1 = \sum_{k=1}^{\mathrm{N}} p_k'$$

$$\mathrm{I}_{\alpha}\left(\frac{\mathrm{Q}}{\mathrm{P}}\right) = \frac{1}{\alpha - 1} \log \frac{\sum_{k=1}^{\mathrm{N}} \mathrm{A}q_k' \left(\frac{\mathrm{A}q_k'}{\mathrm{B}p_k'}\right)^{\alpha-1}}{\sum_{k=1}^{\mathrm{N}} \mathrm{A}q_k'}$$

$$= \frac{1}{\alpha - 1} \log \left(\frac{\mathrm{A}}{\mathrm{B}}\right)^{\alpha-1} + \frac{1}{\alpha - 1} \log \frac{\sum_{k=1}^{\mathrm{N}} q_k' \left(\frac{q_k'}{p_k'}\right)^{\alpha-1}}{\sum_{k=1}^{\mathrm{N}} q_k'}.$$

From what we proved in Section 5, the second term is positive. If $\mathrm{A} \geqslant \mathrm{B}$, the first term is also non-negative and as such $\mathrm{I}_{\alpha}(\mathrm{Q/P})$ is always positive except when $p_k = q_k$. If $\mathrm{A} < \mathrm{B}$, the first term is negative and $\mathrm{I}_{\alpha}(\mathrm{Q/P})$ may be positive or negative.

7. MONOTONIC CHARACTER OF $\mathrm{I}_{\alpha}^{\beta}(\mathrm{Q/P})$

For a fixed β, the proof of Section 5 applies except that here we replace a_k by q_k^{B} and so we have

$$\frac{d}{d\alpha}\left[\mathrm{I}_{\alpha}^{\beta}\left(\frac{\mathrm{Q}}{\mathrm{P}}\right)\right] > 0$$

so that for every fixed value of β, the information of order α and type β is monotonic increasing. Again

$$I_0^{\beta}\left(\frac{Q}{P}\right) = -\log \frac{\sum\limits_{k=1}^{N} q_k^{\beta}\left(\frac{p_k}{q_k}\right)}{\sum\limits_{k=1}^{N} q_k^{\beta}}.$$

If all $p_k/q_k > 1$, this is negative; if all $p_k/q_k < 1$, this expression is positive, but if some are greater than and other less than unity, then this expression can be positive or negative. When

$$\sum_{k=1}^{N} p_k q_k^{\beta-1} < \sum_{k=1}^{N} q_k^{\beta},$$

the information of order α and type β will always be positive.

Again consider

$$I_1^{\beta}\left(\frac{Q}{P}\right) = \frac{\sum\limits_{k=1}^{N} q_k^{\beta} \log \frac{q_k}{p_k}}{\sum\limits_{k=1}^{N} q_k^{\beta}}$$

$$\frac{d}{d\beta}\left[I_1^{\beta}\left(\frac{Q}{P}\right)\right]$$

$$= \frac{1}{\left(\sum\limits_{k=1}^{N} q_k^{\beta}\right)^2}\left\{\sum_{k=1}^{N} q_k^{\beta} \sum_{k=1}^{N} q_k^{\beta} (\log q_k)^2 - \left(\sum_{k=1}^{N} q_k^{\beta} \log q_k\right)^2\right.$$

$$- \sum_{k=1}^{N} q_k^{\beta} \sum_{k=1}^{N} q_k^{\beta} \log q_k \log p_k$$

$$\left. + \sum_{k=1}^{N} q_k^{\beta} \log p_k \sum_{k=1}^{N} q_k^{\beta} \log q_k\right\}.$$

The first two terms are $\geqslant 0$, but the last two terms can change sign.

If $\log p_k = A \log q_k$ and $A < 1$, then the whole expression is positive and the information is a monotonic increasing function of β. If $A > 1$, then this expression is negative and the information in a monotonic decreasing function of β. No completely general statement about the monotonic character of information of order 1 and type β can however be made.

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ON NEGATIVE CHARACTER OF INFORMATION

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ABSTRACT

The article puts forth a hypothesis of negative information which identifies increase of uncertainty with negative character of information. An attempt is made to give a measure of the property without attaching significance to the meaning of the information. The significance of the concept is sought to be related to the field of artificial intelligence and Self-organising Systems within the broader field of computers.

BRILLOUIN[1] has pointed out that the present theory of communication does not take care of the negative character of information since the latter derives itself out of a consideration to the "meaning" or the "value" of information whereas under information theory we consider only the quantum of information. Distinction is made between free information, which occurs when the possible cases are regarded as abstract and have no specified physical significance, and bound information, which occurs when the possible cases can be interpreted as complexions of a physical system. Only in case of bound information, a connection between information and negentropy is considered. Initially, if the number of complexions is P_0, the bound information is $I_{b0}=0$ and the entropy is $S_0=K\,ln\,P_0$. Finally, if the number of complexions is $P_1 < P_0$, the bound information is $I_{b1} \neq 0$ and the entropy is $S_1=K\,ln\,P_1$. Evidently, in this scheme, the system is not isolated, the entropy is decreased when information is obtained, reducing the number of complexions, and this information must be furnished by some external agent whose entropy will increase. The relation between the decrease in entropy of our system and the required information is

$$I_{b1} = K\,(ln\,P_0 - ln\,P_1) = S_0 - S_1 \tag{1}$$

$$S_1 = S_0 - I_{b1} \tag{2}$$

or

We can say that

$$\text{Bound Information} = \text{Decrease in Entropy S} = \text{Increase in Negentropy N} \quad (3)$$

We also like to put down here Shannow's measure of information, according to which the information content of a message equals the amount of uncertainty removed by that message, thus if the message is very rare, the presence of it removes greater amount of uncertainty and its information content is greater than of a message that is less rare than this message. If the probability of this message is P, its information content is

$$I(x) = -\log_2 P \quad (4)$$

and average information content per message out of several ones is

$$H = -\sum_i P_i \log_2 P_i. \quad (5)$$

Also, it is stipulated that

$$I(x) = 0 \quad \text{if} \quad P = 0.$$

NEGATIVE INFORMATION

An example of negative information given by Brillouin[1] does not appeal to me. According to that example if a professor, at the end of his one-hour talk, says, "Excuse me, this was all wrong," this sentence is negative information because it destroys all the information the professor gave during the one hour of his talk. To my mind, this sentence is a positive information because it makes it certain that all the professor said earlier was definitely wrong. The last sentence leads towards certainty and is positive information since removal of uncertainty or addition of certainty is the essential character of positive information. Let me define Negative information as "increase of uncertainty" just as we define positive information as "decrease of uncertainty". In other words, we may say that if an information increases the entropy of our system we call it negative information and its quantitative measure equals the increase in entropy of the system. Following the argument in terms of number of physical complexions, at the beginning let the number of physical complexions be P_0 and an incoming information increase the number to P_1 where $P_1 > P_0$. The required information, then, is

$$I_{b1} = K(ln\,P_0 - ln\,P_1) = -K \log_e \frac{P_1}{P_0}$$

which is negative since $P_1 > P_0$.

Viewing negative information from another angle, let me examine the effect of a piece of information on the probability distribution of a group of other pieces of information. In other words, I am trying to enter the concept of negative information through its effect on probability of the given message and hence its information content. Suppose there were X alternative methods to try a solution to some given problem and a professor picks up one of them successfully in his lecture. The information content is $-\log_2(x^{-1})$, assuming that he has no preference to any particular alternatives. If after the lecture he says that the alternative he picked up was not correct, the information content of this announcement is obviously $-\log_2(x - 1/x)$ which again is positive and not equal to the information it has supposedly destroyed. In this same illustration, suppose the professor initially picked up an alternative which, according to him, had a probability of success $1/y$, where $y < x$. The information content is clearly $-\log_2 y^{-1} = \log_2 y$. At the end of his lecture he discovers that the alternative picked up by him would be no better than any other. This announcement changes the uncertainty connected with his earlier choice and in fact with all or several other choices. The probability of success of his choice becomes $1/x$ and its information content is $\log_2 x$. The announcement, therefore, increases uncertainty associated with that choice by an amount $\log_2(x/y)$ and is negative information of that magnitude. It is significant to point out here that we are not using this information to predict our future likely choice but that this information has only changed our confidence or the information content of our initial choice. We call it negative information since it increased the uncertainty associated with our initial choice. Had this additional information confirmed that our initial choice was definitely wrong, we would have called it positive information since it is confirmatory in nature, like the elimination tests in chemical analysis.

Let me take another example. Suppose messages are being received on four frequencies f_1, f_2, f_3, f_4 (carrier frequencies) and the reception is by way of random pick up of these frequencies at any instant. Let the frequency of interest be f_1. If no extraneous source is trying to confuse messages on

f_1, the probability of receiving a message on f_1 is $\frac{1}{4}$ and the information content is $-\log_2 \frac{1}{4} = 2$ bits. However, if an extraneous source is also sending a message, different from the genuine message (in appearance and not attaching any importance to the meaning), on f_1, the probability of receiving a genuine message on f_1 becomes $\frac{1}{8}$. (One may immediately point out that in so far as information theory is concerned the probability of receiving message on f_1 equals the probability of receiving f_1 itself or when broken down to bits, the information will be equal to sum of the bits in the two messages since no significance is attached to the sense or the meaning of the messages. My clarification is that we expect only one set of symbols in a time whereas we find that there are two sets of symbols being received on frequency f_1, both the sets are such as are admissible in the code we have chosen. Thus our original message to be received has been made ambiguous and doubtful by a probability factor of $\frac{1}{2}$, we may call it a confusion-factor or ambiguity-factor). That means the amount of uncertainty associated with a messsage on f_1 has increased, increasing its information content from $-\log_2 \frac{1}{4}$ to $-\log_2 \frac{1}{8}$, *i.e.*, from 2 bits to 3 bits. Let us, then, define the confusion-factor CF or the ambiguity-factor of decoy-messages as follows:

$$\text{CF} = \frac{\text{Entropy of the message with decoy} - \text{Entropy of original message}}{\text{Entropy of original message}}$$

$$= \frac{\text{Increase in Entropy of the message due to decoy}}{\text{Entropy of Original message}}$$

$$\text{CF} = \frac{\text{Negative information content of decoy message}}{\text{Information content of original message}}.$$

With reference to the above example, the information content of the decoy message is

$$I_b = -\log_2 4 - \log_2 8 = -1 \text{ bit}$$

or else,

$$= k(\log_n 4 - \log_n 8) = -k \log_n 2.$$

Still another example might be taken to illustrate that it is the addition to the uncertainty, rather than destruction or negation of a given information, that means negative information. Suppose a person shoots down a culprit and thinks him to be dead. After several days he is told that the culprit he shot at was not dead. This new information is not negative. If, however, after several days he comes across an identical face (with that of the culprit) he is immediately in doubt, and the simplest calculation would show that this information is $-k \log_n 2$, *i.e.*, $k(\log_n 1 - \log_n 2)$, or else -1 bit since it increases the information content by an amount $-\log_2 \frac{1}{2}$. I must remark that I am trying to avoid any consideration to the meaning of an information but how far I am successful in that attempt is for the reader to judge. This negative character of information enters by way of increasing the number of physical complexions in our system. Of course, taking into account the meaning also, the amount of uncertainty and ambiguity generated by the second information is enormous. A measure of this uncertainty taking meaning also into account could be visualised as the number of possible alternatives that need to be examined before finally giving a verdict on the validity or otherwise of the original information about which uncertainty has been generated. Alternately, the uncertainty may be measured as the number of alternatives to be examined or additional information required in order to modify the earlier information in the given context. At times, the context itself is changed as a result of some information. In this section, however, I have tried to consider the concept of negative information without regard to the meaning of it.

NEGATIVE INFORMATION AND ARTIFICIAL INTELLIGENCE

In the preceding section I have tried to bring out that negative information content of an information could be associated with what I have called "Confusion-factor" or "ambiguity-factor". This aspect is quite relevant to the context of artificial intelligence. On the one hand, a machine (or a person) with fixed probability distribution over its various functional characteristics cannot generate fresh intelligence (*i.e.*, fresh logical dexterity) and, therefore, introducing a certain amount of negative information or a confusion-factor into the machine (or the person) could result in fresh intelligence for the machine or the person since it will have to generate from within, or look up from without, additional information to dispel the ambiguity produced by the negative information. On the other hand, one could use negative information or the confusion-factor to test the intelligence stored in a machine since according to psychologists, there is a correlation between ambiguity-tolerance and intelligence. This suggests that if we can devise clear cut quantitative measure of negative information, we could measure quantitatively the amount of intelligence we have been able to store in an artificial-intelligence designed by us—at least we could compare quantitatively the intelligence stored in two or more artificial-intelligent machines.

CONCLUDING REMARKS

An excellent theory of information has been developed on the consideration of "removal of uncertainty" resulting in a quantitative measure of positive information. Probably, it might be possible to build up a theory of information based on "addition of uncertainty" resulting in a quantitative measure of "negative information" and an associated "confusion-factor". In any case, any attempt to do the latter would be worthwhile since to a machine that has an intelligence built into it, it is equally important, if not more, to assess its shortcomings (by facing confusion or ambiguity) as it is to assess its capabilities (to dispel uncertainty); Also the concept might lead to a measure of quantitative comparison of the intelligence stored into different artificial-intelligent machines. Who knows, we might be able to design "Confusion-generators" or "ambiguity-generators" to test artificially intelligent machines or to help them to acquire fresh intelligence which could be quantitatively assessed !

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STUDIES ON *O*-VANILLINOXIME AS AN ANALYTICAL REAGENT

Part II. Gravimetric Determination of Copper and Nickel and Their Separation from Other Metals

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(Communicated by Prof. T. R. Seshadri, F.A.SC., F.R.S.)

Abstract

o-Vanillinoxime has now been used for the gravimetric determination of copper and nickel alone and in presence of many foreign ions. Copper can be estimated in presence of appreciable amounts of cadmium, zinc, cobalt and lead. The interference due to iron (III), antimony (III), bismuth (III) and tin (II) can be removed by suitable masking agents. Determination of copper and nickel in presence of each other has also been carried out.

Introduction

A large number of ortho-phenolic aldoximes and ketoximes[1–7] have been used as analytical reagents. Among them, salicylaldoxime and its derivatives, *o*-hydroxyacetophenoneoxime and 2-hydroxy-5-methyl-propiophenoneoxime have been employed as reagents for gravimetric determination of nickel, copper and palladium. It has now been observed that copper and nickel form greyish-white and green precipitates respectively with *o*-vanillinoxime and are quantitatively precipitated in the pH range of 2·5 to 9·5 and 5·0 to 10·0 respectively. Cobalt also forms a red-brown complex, which could not be quantitatively precipitated owning to its solubility in aqueous-ethanol. Cadmium is not precipitated until the solution is neutral or slightly basic. Consequently, copper can be separated from cadmium by appropriate control of pH. Separation of lead has also been carried out using an acetate buffer as the lead complex is appreciably soluble in acetate medium and is not quantitatively precipitated in the acidic range of pH. Strict control of pH (2·5–3·0) has been found to be essential in the separation of copper from nickel. The present communication deals mainly with the gravimetric estimation of copper and nickel in presence of many diverse ions.

DISCUSSION

A large number of organic and inorganic precipitants employed for the gravimetric estimation of copper and nickel have been reviewed by Erdey.[8] The thiocyanate method for the estimation of copper suffers from the disadvantage of a low conversion factor and takes a very long time (~6 hours) for complete precipitation of copper. *o*-Vanillinoxime is superior to salicylaldoxime[9] as the precipitate in the case of the latter cannot be digested above 80° C due to the decomposition of the reagent, which results in the contamination of the precipitate and compares favourably with dimethylglyoxime for the estimation of nickel.

EXPERIMENTAL

o-Vanillinoxime was prepared by refluxing recrystallised *o*-vanillin (Fluka) with hydroxylamine hydrochloride and the product melting at 123° C was employed as a 1·0% (w/v) solution in ethanol for the subsequent studies.

Effect of pH and excess reagent.—This was studied in an aqueous solution containing nickel or copper ions in a total volume of ~150 ml. pH was adjusted with acetic acid and ammonia in the presence of ten-fold excess of the reagent. The quantitative precipitation range of pH, where the complex has a stoichiometric composition (metal : reagent = 1 : 2) has been found to be 2·5–9·5 in the case of copper and 5·0–10·0 in the case of nickel. Then investigations were made to determine the minimum amount of reagent required for the complete precipitation of these metal ions; twice the theoretical amount of the reagent is sufficient for quantitative precipitation.

ANALYSIS OF THE COMPLEXES

The complexes were analysed for their metal content. The calculations were made for the formation of 1 : 2 complexes. The results are given below:

(i) Copper complex: (Calc., Cu = 15·02% ; Found Cu = 15·03%)

(ii) Nickel complex: (Calc., Ni = 16·05% ; Found Ni = 16·15%).

Procedure.—The pH of the aqueous solution containing 5–35 mg of nickel or copper was adjusted to a predetermined pH value (as found from the above studies). The solution was heated on a boiling water bath and slightly more than twice the theoretical amount of the reagent was added gradually and with constant stirring. The precipitate was allowed to coagulate on the water bath for half-an-hour. It was then filtered hot through a sintered glass crucible (G–4), washed with 20–30% warm alcohol till the filtrate gave no violet colour with ferric ions and finally with hot water. It was then dried at 120–150° C to constant weight. The results were calculated using conversion factors 0·1605 and 0·1502 for copper and nickel respectively. Some representative results are recorded in Table I.

TABLE I

Copper : pH of the solution = 3·0; *Nickel :* pH of the solution = 5·5

Metal	Amount of the metal ion (mg) taken	Amount of complex (mg)	Amount of metal ion found (mg)	Error (mg)
Copper ..	6·35	39·50	6·34	−0·01
	12·70	79·25	12·72	0·02
	19·05	118·80	19·07	0·02
	25·40	158·50	25·44	0·04
	31·75	198·00	31·78	0·03
Nickel ..	6·47	43·00	6·46	−0·01
	12·94	86·30	12·96	0·02
	19·41	129·45	19·44	0·03
	25·88	172·60	25·92	0·04
	32·35	215·60	32·39	0·04

STUDY OF INTERFERENCES

The interference due to various cations and anions has been studied. Wherever possible, the interference has been eliminated with suitable masking agents or by adjustment of pH. Copper and nickel have been estimated at pH 3·0–4·0 and 5·5 respectively, unless otherwise specified. Interference due to iron (III), antimony (III), and bismuth (III) has been removed by working at pH 4·0 in the case of copper and at pH 8·0 in the case of nickel in the presence of ~1·0 g. sodium potassium tartrate, which otherwise does not interfere in the determination. Equivalent amounts of sodium fluoride have been used to mask tin (II). Twenty-fold excess of phosphate and borate can be tolerated in the estimation. Results of some of the separations of copper or nickel from other ions are shown in Table II and are in fair agreement with the theoretical values.

TABLE II

Cu (II) taken = 6·36 *mg*; *Ni (II) taken* = 6·47 *mg*

Foreign metal ions	Amount of foreign metal ions	Amount of the complex		Amount of the metal found	
		Cu (II) complex	Ni (II) complex	Cu (II)	Ni (II)
	(mg)	(mg)	(mg)	(mg)	(mg)
Co (II) ..	115·00	39·70	43·20	6·37	6·49
Zn (II) ..	150·00	39·65	43·15	6·36	6·48
Pb (II) ..	104·50	39·80	43·10	6·39	6·47
Mn (II) ..	110·00	39·60	43·10	6·37	6·47
Cd (II) ..	500·00	39·60	43·10	6·36	6·47
Fe (III)‡*	100·00	39·50	43·00	6·34	6·46
Fe (II) ..	84·00	39·60	43·00	6·36	6·46
Mg (II) ..	105·00	39·80	43·15	6·39	6·48
UO_2 (II) ..	150·00	39·60	43·20	6·36	6·49
Sn (II)† ..	60·00	39·50	43·00	6·34	6·46
Ag (I) ..	50·00	39·70	43·10	6·37	6·47
Bi (III)‡ ..	100·00	39·60	..	6·36	..
Sb (III) ..	60·80	39·65	43·00	6·36	6·46
Mo (VI) ..	100·00	39·80	43·20	6·39	6·49
W (VI) ..	112·00	39·90	43·25	6·40	6·50
Se (IV) ..	80·00	39·50	42·95	6·34	6·45
Te (IV) ..	125·00	39·50	42·95	6·34	6·45

* Masked by citrate ions (sodium citrate).

† Masked by equivalent amount of fluoride ions (sodium fluoride).

‡ Masked by equivalent amount of tartrate ions (sodium potassium tartrate).

Determination of copper and nickel in presence of each other.—This has been carried out in synthetic mixtures. Copper is precipitated at a pH 2·5 and estimated as described earlier. The filtrate is concentrated to ~150 ml. and nickel is precipitated by raising the pH to 8·5 after adding a desired amount of the reagent. Some of the results are shown in Table III.

TABLE III

Wt. of Cu (II) taken	Wt. of Ni (II) taken	Wt. of Cu (II) complex	Wt. of Ni (II) complex	Wt. of Cu (II) found	Wt. of Ni (II) found	Error for Cu (II)	Error for Ni (II)
(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)
6·35	32·35	39·50	215·6	6·34	32·39	−0·01	0·04
12·70	25·88	79·30	172·4	12·73	25·89	0·03	0·01
19·05	19·41	118·80	129·2	19·07	19·40	0·02	−0·01
25·40	12·94	158·45	86·20	25·43	12·95	0·03	0·01
31·75	6·47	198·10	42·95	31·79	6·45	0·04	−0·02

This method can thus be recommended for the analysis of cupro-nickel alloys.

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SEPARATION AND GRAVIMETRIC DETERMINATION OF IRON USING OXIMIDOBENZOTETRONIC ACID

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Abstract

Using oximidobenzotetronic acid (OBTA) as a reagent, iron (II) has been separated and accurately determined gravimetrically in presence of 10-fold or more of Mn (II), Al (III), Cr (III), Ti (IV), Zr (IV), Th (IV), Ni (II), Zn (II), Mo (VI), Ca (II) Mg (II), tartrate, citrate, acetate, phosphate, sulphocyanide, fluoride W (VI), Cu (II), Bi (III) and Sn (II). Ce (IV), Ce (III), Co (II), V (V) and EDTA, however, interfere in the determination.

Introduction

A large number of reagents have been suggested for the separation and gravimetric determination of iron in presence of other ions.[1–3] There is, however, hardly any reagent that can be used for the separation and accurate determination of iron in presence of large quantities of alkaline earth metal ions, copper (II), aluminium (III), chromium (III), manganese (II), molybdenum (VI), tungsten (VI), titanium (IV), zirconium (IV), thorium (IV), bismuth (III) and tin (II) without resorting to repeated precipitations.

Oximidobenzotetronic acid (OBTA) has already been used for the gravimetric determination of cobalt (II)[4] and palladium (II)[5] and for the spectrophotometric determination of iron (II),[6] cobalt (II)[7], ruthenium (III)[8] and rhodium (III).[8] With iron (III) an ethanolic or acetonic solution of the reagent slowly forms a blue solution which on prolonged keeping (about 1 hr.) in presence of ammonium salts (about 5 gm.) forms a precipitate but the reaction is not quantitative. Under similar conditions, however, iron (II) is quantitatively precipitated. The present communication deals with the investigations on the use of OBTA for the separation and gravimetric determination of iron (II) in presence of other ions.

EXPERIMENTAL

Reagent and chemicals.—Oximidobenzotetronic acid (OBTA) was prepared as described earlier.[4] A freshly prepared solution of the reagent in 25% aqueous ethanol or acetone was used for all the determinations.

Stock solution of iron (II) was prepared by using ammonium ferrous sulphate (E. Merck, pro-analysi) and was standardised as Fe_2O_3 after precipitation as hydroxide. Hydroquinone (B.D.H., L.R.) solution was used to keep iron in ferrous state. Dilute solutions of hydrochloric acid and potassium hydroxide were used for the adjustment of pH, which was measured with a Beckman pH meter model H–2 using suitable glass electrode.

Determination of iron (II) by OBTA.—To about 100 ml. of iron (II) solution containing 10–45 mg. Fe_2O_3 and 5 g. ammonium nitrate or chloride at pH 1·7, the reagent was slowly added with constant stirring till 10 mg. of OBTA per mg. Fe_2O_3 had been added. The solution was kept at room temperature (30°) for about 1 hr. and the resultant precipitate allowed to settle. The yellow supernatant solution was filtered through a Whatman filter-paper No. 40. Any precipitate sticking to the beaker was transferred to the filter-paper using 2 N hydrochloric acid containing 10% ammonium nitrate. The precipitate was washed with the $HCl–NH_4NO_3$ mixture till free from sulphate ions, dried in hot air and then ignited to Fe_2O_3 and weighed. Results of some of the determinations are shown in Table I.

TABLE I

Determination of iron (II) by OBTA

Fe_2O_3 taken mg.	Fe_2O_3 found mg.	Difference mg.
1·50	1·40	0·10
3·00	2·95	0·05
4·50	4·40	0·10
9·05	9·10	0·05
15·10	15·10	0·00
21·60	21·55	0·05
32·40	32·30	0·10
43·20	43·20	0·00

The deep blue complex is soluble in water, ethanol, acetone, chloroform or dilute mineral acids giving a blue solution, but is insoluble in 5% ethanol or 2 N mineral acid each containing 10% or more of ammonium nitrate. The complex is not extracted into toluene, benzene or ether.

Effect of pH on the precipitation of iron (II)–OBTA complex.—It has been observed that iron (II) can be accurately determined when after the addition of the reagent, the pH is maintained at 0·8–9·0. At higher or lower pH values, the precipitation of the complex is incomplete.

Separation and determination of iron (II) in presence of other ions.—It has been found that iron (II) can be successfully separated and determined in presence of 10-fold amounts or more of the following ions at pH 1·7–2·0 in a single precipitation by the procedure described above (Table II): manganese (II), aluminium (III), chromium (III), titanium (IV), zirconium (IV), thorium (IV), nickel (II), zinc (II), molybdenum (VI), calcium (II), magnesium (II), tartrate, citrate, acetate, phosphate, fluoride and sulphocyanide. The interference due to copper (II), bismuth (II), tin (II) and tungsten (VI) could be eliminated by carrying out the determination in presence of tartaric acid (Table II). However, cobalt (II), vanadium (V), cerium (IV), cerium (III) and EDTA have been found to interfere with the above determination.

TABLE II

Determination of iron (II) in presence of foreign ions

Weight of Fe_2O_3 taken for each determination = 15·10 mg. (≡ 10·57 mg. of Fe)

Foreign ion taken	Amount mg.	Wt. of Fe_2O_3 found mg.
1. Mn (II) as $MnSO_4.4\,H_2O$ ..	17·63	15·15
	77·99	15·20
	148·8	15·05
2. Al (III) as $KAl\,(SO_4)_2.12\,H_2O$ ..	15·52	15·15
	57·31	15·15
	144·90	15·10
3. Cr (III) as $Cr\,(NO_3)_3.9\,H_2O$ ..	13·09	15·10
	73·78	15·10
	140·96	15·00
4. Ti (IV) as $TiCl_4$	27·16	15·05
	54·32	15·15
	81·48	15·15

TABLE II—*Contd.*

Foreign ion taken	Amount mg.	Wt. of Fe_2O_3 found mg.
5. Zr (IV) as $ZrOCl_2.8\,H_2O$ ..	86·88	15·20
	182·4	15·05
6. Th (IV) as $Th\,(NO_3)_4.6\,H_2O$ ..	131·7	15·20
	363·9	15·20
7. Ni (II) as $NiSO_4.7\,H_2O$ ..	13·86	15·15
	43·99	15·10
	138·5	15·15
8. Zn (II) as Zn metal ..	245·20	15·15
	653·95	15·20
9. Mo (VI) as $(NH_4)_6\ Mo_7O_{24}.4\,H_2O$	21·55	15·15
	70·15	15·15
	115·25	15·10
10. Ca (II) as $CaCO_3$ ..	20·96	15·15
	152·40	15·20
11. Mg (II) as $MgSO_4.7\,H_2O$ ..	79·95	15·20
	166·00	15·15
12. Tartrate as $[CH\,(OH)\,COOH]_2$	14·26	15·20
	174·6	15·10
	246·5	15·15
13. Citrate as citric acid ..	95·70	15·00
	235·00	15·00
14. $CH_3CO_2^-$ as $CH_3CO_2Na.3\,H_2O$..	46·85	15·10
	121·8	15·20
15. PO_4^{-3} as $(NH_4)_2\,HPO_4$ ..	13·67	15·15
	63·12	15·05
	193·3	15·20
16. SCN^- as KSCN ..	30·28	15·10
	185·1	15·20
17. F^- as NH_4F ..	53·53	15·20
	147·9	15·15
18. Cu (II) as $CuSO_4.5\,H_2O$ ..	7·52	15·05*
	154·6	15·20*
19. Bi (III) as $Bi\,(NO_3)_3.5\,H_2O$ ..	61·25	15·20*
	93·58	15·15*
20. Sn (II) as $SnCl_2.2\,H_2O$ ..	78·31	15·20*
	162·40	15·10*
21. W (VI) as $Na_2WO_4.2\,H_2O$ ..	15·20	15·20*
	15·05	15·05*

* Determination done in presence of 1 g. tartaric acid.

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UNSTEADY COUETTE FLOW OF A CONDUCTING FLUID BETWEEN TWO PARALLEL PLATES UNDER A TRANSVERSE MAGNETIC FIELD—II

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ABSTRACT

The effect of a sudden change in magnetic field and pressure gradient on a steady Couette flow of a viscous incompressible fluid between two parallel plates in the presence of a transverse magnetic field is considered. Expressions for the velocity of the fluid in the disturbed flow, the intensities of the electrical and magnetic fields are obtained in two cases when the plates are non-conducting and when they are perfectly conducting.

1. INTRODUCTION AND BASIC EQUATIONS

WE propose to examine the transient flow caused by disturbing the steady state obtained in the preceding paper (hence after called as Part I) by a sudden change in magnetic field from H_0 to αH_0 and in pressure gradient from P to βP. A similar problem has been discussed by Rathi (1963) for Hartmann flow. The equations (2.6) of Part I become for the disturbed flow,

$$\frac{\partial u}{\partial t} = \beta P + \frac{1}{R}\frac{\partial^2 u}{\partial y^2} + \frac{\alpha M^2}{RR_m}\frac{\partial h}{\partial y},$$

$$\frac{\alpha M^2}{RR_m} h \frac{\partial h}{\partial y} = -\frac{\partial p}{\partial y},$$

$$\frac{\partial h}{\partial t} = \frac{1}{R_m}\frac{\partial^2 h}{\partial y^2} + \alpha\frac{\partial u}{\partial y},$$

$$\frac{\partial h}{\partial y} = -R_m(\alpha u + e). \tag{1.1}$$

We suppose that the change occurs at $t = 0$, so that for $t \leqslant 0$ the flow is determined by the steady state solutions u_0, h_0 and e_0 for the velocity of the fluid, the induced magnetic field and the electrical intensity. We seek the solutions of equations (1.1) subject to certain initial conditions at $t = 0$ (the steady state solutions in Part I) and the boundary conditions for $t > 0$ (*see* § 3 of Part I).

2. SOLUTION OF THE EQUATIONS

We limit ourselves to determine u, h and e only, whence the pressure p can be determined by the second equation of (1.1). Taking the Laplace transform of (1.1) subject to the initial conditions

$$s\bar{u} = \frac{\beta P}{s} + \frac{1}{R}\frac{d^2\bar{u}}{dy^2} + \frac{\alpha M^2}{RR_m}\frac{d\bar{h}}{dy} + u_0,$$

$$s\bar{h} = \frac{1}{R_m}\frac{d^2\bar{h}}{dy^2} + \alpha\frac{d\bar{u}}{dy} + h_0,$$

$$\frac{d\bar{h}}{dy} = -R_m(\alpha\bar{u} + \bar{e}). \tag{2.1}$$

Case 1.—The plates are non-conducting.

u_0, h_0 and e_0 are given by (4.25–4.27) of Part I. Eliminating $\bar{h}$, we get

$$\frac{d^4\bar{u}}{dy^4} - \{s(R + R_m) + \alpha^2M^2\}\frac{d^2\bar{u}}{dy^2} + s^2RR_m\bar{u} = (\beta - \alpha)PRR_m$$
$$+ \frac{PRX_1}{M}\frac{\text{chM}y}{\text{shM}} - X_1\frac{\text{shM}y}{\text{shM}} + \frac{sPR^2R_m}{M}\coth M, \tag{2.2}$$

where

$$X_1 = \alpha M^2R_m + M^2R - sRR_m. \tag{2.3}$$

Solving this equation for $\bar{u}$, we get

$$\bar{u} = c_1\text{ch}my + c_2\text{sh}my + c_3\text{ch}ny + c_4\text{sh}ny + \frac{PRX_1}{MX}\frac{\text{chM}y}{\text{shM}}$$
$$+ \frac{PR}{sM}\coth M - \frac{X_1}{X}\frac{\text{shM}y}{\text{shM}} + \frac{\beta - \alpha}{s^2}P, \tag{2.4}$$

where c_1, c_2, c_3 and c_4 are arbitrary constants of integration and

$$m = \tfrac{1}{2}\{\sqrt{\alpha^2M^2 + (\sqrt{R} + \sqrt{R_m})^2 s}$$
$$+ \sqrt{\alpha^2M^2 + (\sqrt{R} - \sqrt{R_m})^2 s}\}, \tag{2.5}$$

$$n = \tfrac{1}{2}\{\sqrt{\alpha^2 M^2 + (\sqrt{R} + \sqrt{R_m})^2 s} - \sqrt{\alpha^2 M^2 + (\sqrt{R} - \sqrt{R_m})^2 s}\}, \tag{2.6}$$

$$X = M^4 (1 - \alpha^2) - sM^2 (R + R_m) + s^2 R R_m. \tag{2.7}$$

Substituting $\bar{u}$ in (2.1)

$$\bar{h} = \frac{K_1 R R_m}{\alpha M^2}(c_1 \mathrm{sh} my + c_2 \mathrm{ch} my) + \frac{K_2 R R_m}{\alpha M^2}(c_3 \mathrm{sh} ny + c_4 \mathrm{ch} ny) + \frac{R_m}{sM}\coth M - \frac{P R R_m y}{sM^2} - \frac{P R R_m}{M^2}\frac{X_2}{X}\frac{\mathrm{sh} My}{\mathrm{sh} M} + \frac{R_m X_2}{MX}\frac{\mathrm{ch} My}{\mathrm{sh} M}. \tag{2.8}$$

$\bar{e}$ is then given by

$$-\bar{e} = \frac{sR - m^2 + \alpha^2 M^2}{\alpha M^2}(c_1 \mathrm{ch} my + c_2 \mathrm{sh} my) + \frac{sR - n^2 + \alpha^2 M^2}{\alpha M^2} \times (c_3 \mathrm{ch} ny + c_4 \mathrm{sh} ny) + \left\{\frac{PR}{MX}\frac{\mathrm{ch} My}{\mathrm{sh} M} - \frac{\mathrm{sh} My}{X \mathrm{sh} M}\right\}(\alpha X_1 - X_2) + \frac{PR}{sM}\left(\alpha \coth M - \frac{1}{M}\right) + \frac{\alpha(\beta - \alpha)}{s^2} P, \tag{2.9}$$

where K_1 and K_2 are defined by (4.10) of Part I and

$$X_2 = \alpha M^2 R + M^2 R_m - sRR_m. \tag{2.10}$$

We determine the arbitrary constants c_1, c_2, c_3 and c_4 in (2.4, 2.8, 2.9) using the boundary conditions (4.11) of Part I.

$$\bar{u} = \frac{P}{\triangle_1}(F_1 \mathrm{ch} my - G_1 \mathrm{ch} ny) + \frac{1}{\triangle_2}(G_2 \mathrm{sh} ny - F_2 \mathrm{sh} my) + \frac{PRX_1}{MX}\frac{\mathrm{ch} My}{\mathrm{ch} M} + \frac{PR \coth M}{sM} - \frac{X_1}{X}\frac{\mathrm{sh} My}{\mathrm{sh} M} + \frac{\beta - \alpha}{s^2}, \tag{2.11}$$

$$\bar{h} = \frac{PRR_m}{\alpha M^2 \triangle_1}(K_1 F_1 \mathrm{sh} my - K_2 G_1 \mathrm{sh} ny) + \frac{R_m}{sM}\coth M - \frac{PRR_m y}{sM^2} + \frac{RR_m}{\alpha M^2 \triangle_2}(K_2 G_2 \mathrm{ch} ny - K_1 F_2 \mathrm{ch} my) - \frac{PRR_m}{M^2}\frac{X_2}{X}\frac{\mathrm{sh} My}{\mathrm{sh} M} + \frac{R_m}{M}\frac{X_2}{X}\frac{\mathrm{ch} My}{\mathrm{sh} M}, \tag{2.12}$$

$$
\begin{aligned}
-\bar{e} = {} & \frac{P}{\alpha M^2 \triangle_1}\{(sR - m^2 + \alpha^2 M^2)\, F_1 \mathrm{ch}\, my \\
& - (sR - n^2 + \alpha^2 M^2)\, G_1 \mathrm{ch}\, ny\} \\
& + \frac{1}{\alpha M^2 \triangle_2}\{(sR - n^2 + \alpha^2 M^2)\, G_2 \mathrm{sh}\, ny \\
& - (sR - m^2 + \alpha^2 M^2)\, F_2 \mathrm{sh}\, my\} \\
& + \frac{PR}{MX}\left\{\frac{\mathrm{ch}My}{\mathrm{sh}M} - \frac{\mathrm{sh}My}{X\mathrm{sh}M}\right\}(\alpha X_1 - X_2) \\
& + \frac{PR}{sM}\left(\alpha \coth M - \frac{1}{M}\right) + \frac{\alpha(\beta - \alpha) P}{s^2}, \qquad (2.13)
\end{aligned}
$$

where

$$F_1 = \frac{\alpha(X + sX_2)}{sX}\, \mathrm{ch}\, n + \left\{\frac{\beta - \alpha}{s^2} + \frac{R \coth M}{MsX}\right\}(X + sX_1)\, K_2 \mathrm{sh}\, n, \qquad (2.14)$$

$$G_1 = \frac{\alpha(X + sX_2)}{sX}\, \mathrm{ch}\, m + \left\{\frac{\beta - \alpha}{s^2} + \frac{R \coth M}{MsX}\right\}(X + sX_1)\, K_1 \mathrm{sh}\, m, \qquad (2.15)$$

$$F_2 = \frac{X + sX_1}{sX}\, K_2 \mathrm{ch}\, n + \frac{\alpha M}{R} \coth M\, \frac{X + sX_2}{sX}\, \mathrm{sh}\, n, \qquad (2.16)$$

$$G_2 = \frac{X + sX_1}{sX}\, K_1 \mathrm{ch}\, m + \frac{\alpha M}{R} \coth M\, \frac{X + sX_2}{sX}\, \mathrm{sh}\, m, \qquad (2.17)$$

and $\triangle_1$, $\triangle_2$ are defined by (4.15, 4.16) of Part I.

The functions $\bar{u}$, $\bar{h}$ and $\bar{e}$ have poles at $s = o$, s' and s''.

Writing

$$s = -\frac{\alpha^2 M^2 + \theta^2}{R(1 + r)^2},$$

s' and s'' are determined by roots θ of equations (4.17, 4.19) of Part I where

$$\phi = \sqrt{q^2\theta^2 - (1 - q^2)\,\alpha^2 M^2}. \qquad (2.18)$$

$X = 0$ gives removable singularities. On inverting $\bar{u}$, $\bar{h}$ and $\bar{e}$

$$
\begin{aligned}
u = u_{\text{stat.}} &+ \sum_{s'} \frac{4\mathrm{P}r\theta\phi e^{st}}{\mathrm{Y}'(1+r)^3 s}\Big[\frac{\alpha(\mathrm{X}+s\mathrm{X}_2)}{\mathrm{X}}(\mathrm{ch}n\mathrm{ch}my - \mathrm{ch}m\mathrm{ch}ny) \\
&- \left\{\frac{\beta-\alpha}{s} + \frac{\mathrm{R}\coth\mathrm{M}}{\mathrm{MX}}(\mathrm{X}+s\mathrm{X}_1)\right\}\{(\mathrm{K}_1\mathrm{sh}m\mathrm{ch}ny \\
&- \mathrm{K}_2\mathrm{sh}n\mathrm{ch}my)\}\Big] - \sum_{s''}\frac{4r\theta\phi e^{st}}{s(1+r)^3\mathrm{XY}''} \\
&\times \Big\{(\mathrm{X}+s\mathrm{X}_1)(\mathrm{K}_1\mathrm{ch}m\mathrm{sh}ny - \mathrm{K}_2\mathrm{ch}n\mathrm{sh}my) \\
&- \frac{\alpha\mathrm{M}}{\mathrm{R}}\coth\mathrm{M}(\mathrm{X}+s\mathrm{X}_2)(\mathrm{sh}my\mathrm{sh}n - \mathrm{sh}m\mathrm{sh}ny)\Big\}, \qquad (2.19)
\end{aligned}
$$

$$
\begin{aligned}
h = h_{\text{stat.}} &+ \sum_{s'}\frac{4\mathrm{PR}^2r^3\theta\phi e^{st}}{(1+r)^3 s\mathrm{Y}'}\Big[\frac{\mathrm{X}+s\mathrm{X}_2}{\mathrm{XM}^2}(\mathrm{K}_1\mathrm{ch}n\mathrm{sh}my - \mathrm{K}_2\mathrm{ch}m\mathrm{sh}ny) \\
&- \frac{\alpha}{\mathrm{R}^2r}\left\{\frac{\beta-\alpha}{s} + \frac{\mathrm{R}\coth\mathrm{M}}{\mathrm{MX}}(\mathrm{X}+s\mathrm{X}_1)\right\} \\
&\times(\mathrm{sh}n\mathrm{sh}my - \mathrm{sh}m\mathrm{sh}ny)\Big] - \sum_{s''}\frac{4r^2\theta\phi e^{st}}{(1+r)^3\mathrm{Y}''s\mathrm{X}} \\
&\times\Big[(\mathrm{X}+s\mathrm{X}_1)\,\alpha\,(\mathrm{ch}n\mathrm{ch}my - \mathrm{ch}m\mathrm{ch}ny) \\
&- \frac{\mathrm{R}r\coth\mathrm{M}}{\mathrm{M}}(\mathrm{X}+s\mathrm{X}_2)(\mathrm{K}_1\mathrm{ch}my\mathrm{sh}n - \mathrm{K}_2\mathrm{sh}m\mathrm{ch}ny)\Big], \qquad (2.20)
\end{aligned}
$$

$$
\begin{aligned}
e = e_{\text{stat.}} &- \sum_{s'}\frac{4\mathrm{P}r\theta\phi e^{st}}{\alpha\mathrm{M}^2(1+r)^3 s\mathrm{Y}'}\Big[\frac{\alpha(\mathrm{X}+s\mathrm{X}_2)}{\mathrm{X}} \\
&\times\{(s\mathrm{R}-m^2+\alpha^2\mathrm{M}^2)\,\mathrm{ch}n\mathrm{ch}my - (s\mathrm{R}-n^2+\alpha^2\mathrm{M}^2)\,\mathrm{ch}m\mathrm{ch}ny\} \\
&+ \left\{\frac{\beta-\alpha}{s} + \frac{\mathrm{R}\coth\mathrm{M}}{\mathrm{MX}}(\mathrm{X}+s\mathrm{X}_1)\right\} \\
&\times\{(s\mathrm{R}-m^2+\alpha^2\mathrm{M}^2)\,\mathrm{K}_2\mathrm{sh}n\mathrm{ch}my \\
&- (s\mathrm{R}-n^2+\alpha^2\mathrm{M}^2)\,\mathrm{K}_1\mathrm{sh}m\mathrm{ch}ny\}\Big]
\end{aligned}
$$

$$- \sum_{s''} \frac{4r\theta\phi e^{st}}{(1+r)^3 \mathrm{MR}s\mathrm{XY}''} \Big[\{(s\mathrm{R} - m^2 + \alpha^2\mathrm{M}^2)\, \mathrm{K}_2 \mathrm{ch}n\mathrm{sh}my$$

$$- (s\mathrm{R} - n^2 + \alpha^2\mathrm{M}^2)\, \mathrm{K}_1 \mathrm{sh}ny\mathrm{ch}m\} \frac{\mathrm{X} + s\mathrm{X}_1}{\alpha\mathrm{M}}$$

$$+ \{(s\mathrm{R} - m^2 + \alpha^2\mathrm{M}^2)\, \mathrm{sh}n\mathrm{sh}my - (s\mathrm{R} - n^2 + \alpha^2\mathrm{M}^2)\, \mathrm{sh}m\mathrm{sh}ny\}$$

$$\times \coth \mathrm{M}(\mathrm{X} + s\mathrm{X}_2) \Big], \qquad (2.21)$$

where Y′ and Y″ are defined by (4.21, 4.22) of Part I. The values $u_{\text{stat.}}$, $h_{\text{stat.}}$ and $e_{\text{stat.}}$ in (2.19–2.21) which correspond to stationary conditions are calculated as residues for $s = 0$ and are determined by formulas

$$u_{\text{stat.}} = \frac{\beta\mathrm{PR}}{\alpha\mathrm{M}} \frac{(\mathrm{ch}\alpha\mathrm{M} - \mathrm{ch}\alpha\mathrm{M}y)}{\mathrm{sh}\alpha\mathrm{M}} + \frac{\mathrm{sh}\alpha\mathrm{M}y}{\mathrm{sh}\alpha\mathrm{M}}, \qquad (2.22)$$

$$h_{\text{stat.}} = \frac{\beta\mathrm{PRR}_m}{\alpha\mathrm{M}^2\mathrm{sh}\alpha\mathrm{M}} (\mathrm{sh}\alpha\mathrm{M}y - y\mathrm{sh}\alpha\mathrm{M}) + \frac{\mathrm{R}_m}{\mathrm{M}\mathrm{sh}\alpha\mathrm{M}} (\mathrm{ch}\alpha\mathrm{M} - \mathrm{ch}\alpha\mathrm{M}y), \qquad (2.23)$$

$$e_{\text{stat.}} = \frac{\mathrm{PR}}{\alpha\mathrm{M}^2} (\alpha\mathrm{M} \coth \alpha\mathrm{M} - 1). \qquad (2.24)$$

Case ii.—The plates are perfectly conducting.

u_0 and h_0 are given by (4.40, 4.41) of Part I. $\bar{u}$ satisfies

$$\frac{d^4\bar{u}}{dy^4} - \{s(\mathrm{R} + \mathrm{R}_m) + \alpha^2\mathrm{M}^2\} \frac{d^2\bar{u}}{dy^2} + s^2\mathrm{RR}_m\bar{u}$$

$$= (\beta - \alpha)\, \mathrm{PRR}_m + \frac{s\mathrm{PR}^2\mathrm{R}_m}{\mathrm{M}^2} + \frac{\mathrm{PRX}_1}{\mathrm{M}^2} \frac{\mathrm{ch}\mathrm{M}y}{\mathrm{ch}\mathrm{M}} - \frac{\mathrm{X}_1\mathrm{sh}\mathrm{M}y}{\mathrm{sh}\mathrm{M}}. \qquad (2.25)$$

Solving for $\bar{u}$

$$\bar{u} = c_1\mathrm{ch}my + c_2\mathrm{sh}my + c_3\mathrm{ch}ny + c_4\mathrm{sh}ny + \frac{(\beta - \alpha)\,\mathrm{P}}{s^2} + \frac{\mathrm{PR}}{\mathrm{M}^2 s}$$

$$+ \frac{\mathrm{PRX}_1}{\mathrm{M}^2\mathrm{X}} \frac{\mathrm{ch}\mathrm{M}y}{\mathrm{ch}\mathrm{M}} - \frac{\mathrm{X}_1\mathrm{sh}\mathrm{M}y}{\mathrm{X}\mathrm{sh}\mathrm{M}}, \qquad (2.26)$$

whence, from (2.1)

$$\bar{h} = \frac{K_1RR_m}{\alpha M^2}(c_1\text{sh}my + c_2\text{ch}my) + \frac{K_2RR_m}{\alpha M^2}(c_3\text{sh}ny + c_4\text{ch}ny) - \frac{PRR_my}{sM^2} - \frac{PRR_m}{M^3}\frac{X_2}{X}\frac{\text{sh}My}{\text{ch}M} + \frac{R_m}{sM^2} + \frac{R_m}{M}\frac{X_2}{X}\frac{\text{ch}My}{\text{sh}M}. \qquad (2.27)$$

Determining the constants c_1, c_2, c_3 and c_4 by (4.28) of Part I,

$$\bar{u} = -\frac{PR}{\triangle_3}(F_3\text{ch}my - G_3\text{ch}ny) + \frac{R}{\triangle_4}(F_4\text{sh}my - G_4\text{sh}ny) + \frac{PR}{sM^2} + \frac{PR}{M^2}\frac{X_1}{X}\frac{\text{ch}My}{\text{ch}M} - \frac{X_1}{X}\frac{\text{sh}My}{\text{sh}M}, \qquad (2.28)$$

$$\bar{h} = -\frac{PR^2R_m}{\alpha M^2\triangle_3}(K_1F_3\text{sh}my - K_2G_3\text{sh}ny) + \frac{R^2R_m}{\alpha M^2\triangle_4}(K_1F_4\text{ch}my - K_2G_4\text{ch}ny) - \frac{PRR_my}{sM^2} + \frac{R_m}{sM^2} - \frac{PRR_m}{M^3}\frac{X_2}{X}\frac{\text{sh}My}{\text{ch}M} + \frac{R_mX_2}{MX}\frac{\text{ch}My}{\text{sh}M}, \qquad (2.29)$$

$$\bar{e} = \frac{PR}{\alpha M^2\triangle_3}\{(\alpha^2M^2+sR-m^2)F_3\text{ch}my - (\alpha^2M^2+sR-n^2)G_3\text{ch}ny\} - \frac{R}{\alpha M^2\triangle_4}\{(\alpha^2M^2+sR-m^2)F_4\text{sh}my - (\alpha^2M^2+sR-n^2) \times G_4\text{sh}ny\} - \frac{PR(\alpha-1)}{sM^2} - \frac{\alpha P(\beta-\alpha)}{s^2} + \frac{PR}{M^2}\frac{\text{ch}My}{\text{ch}M} - \frac{\text{sh}My}{\text{sh}M}\frac{(X_2-\alpha X_1)}{X}, \qquad (2.30)$$

where

$$F_3 = \left[nK_2\left\{\frac{(\beta-\alpha)}{s^2} + \frac{R}{M^2}\frac{X+sX_1}{sX}\right\} + \frac{\alpha(X+sX_2)}{sX}\right]\text{ch}n, \qquad (2.31)$$

$$G_3 = \left[mK_1\left\{\frac{(\beta-\alpha)}{s^2} + \frac{R}{M^2}\frac{X+sX_1}{sX}\right\} + \frac{\alpha(X+sX_2)}{sX}\right]\text{ch}m, \qquad (2.32)$$

$$F_4 = \left\{nK_2\frac{X+sX_1}{sX} + \frac{\alpha M^2}{R}\frac{(\alpha X+sX_2)}{sX}\right\}\text{sh}n, \qquad (2.33)$$

$$G_4 = \left\{mK_1\frac{X+sX_1}{sX} + \frac{\alpha M^2}{R}\frac{(\alpha X+sX_2)}{sX}\right\}\text{sh}m, \qquad (2.34)$$

$\triangle_3$ and $\triangle_4$ are defined by (4.32, 4.33) of Part I.

The functions $\bar{u}$, $\bar{h}$ and $\bar{e}$ have poles at $s = o,\ s',\ s''$ whilst

$$X = o,\quad s = -\frac{\alpha^2 M^2}{R(1+r)^2}$$

and

$$s = -\frac{\alpha^2 M^2}{R(1-r)^2}$$

give removable singularities.

Writing

$$s = -\frac{\alpha^2 M^2 + \theta^2}{R(1+r)^2},$$

s' and s'' are determined by

$$\theta = \frac{-k\pi \pm \sqrt{q^2 k^2 \pi^2 - (q^2-1)^2 \alpha^2 M^2}}{q^2 - 1},$$

k assuming odd or even integral values according as s is s' or s''.

On inversion

$$\begin{aligned} u = u_{\text{stat.}} &+ \sum_{s'} \frac{4Pe^{st}}{sZ'(1+r)^2}\left[\left\{\frac{\beta-\alpha}{s} + \frac{R}{M^2}\frac{X+sX_1}{X}\right\}\right. \\ &\times (nK_2 \operatorname{ch} my \operatorname{ch} n - mK_1 \operatorname{ch} m \operatorname{ch} ny) + \frac{\alpha}{X}(X + sX_2) \\ &\left.\times (\operatorname{ch} my \operatorname{ch} n - \operatorname{ch} m \operatorname{ch} ny)\right] - \sum_{s''} \frac{4e^{st}}{sX(1+r)^2 Z''} \\ &\times \Big\{(X+sX_1)(nK_2 \operatorname{sh} my \operatorname{sh} n - mK_1 \operatorname{sh} m \operatorname{sh} ny) \\ &+ \frac{\alpha M^2}{R}(\alpha X + sX_2)(\operatorname{sh} my \operatorname{sh} n - \operatorname{sh} m \operatorname{sh} ny)\Big\}, \end{aligned} \tag{2.35}$$

$$h = h_{\text{stat.}} - \sum_{s'} \frac{4\mathrm{P}re^{st}}{sZ'(1+r)^2}\left[\alpha\left\{\frac{\beta-\alpha}{s} + \frac{\mathrm{R}}{\mathrm{M}^2}\frac{(\mathrm{X}+s\mathrm{X}_1)}{\mathrm{X}}\right\}\right.$$

$$\times\,(n\mathrm{ch}n\mathrm{sh}my - m\mathrm{ch}m\mathrm{sh}ny) - \frac{\mathrm{R}^2r}{\mathrm{M}^2\mathrm{X}}$$

$$\left.\times\,(\mathrm{X}+s\mathrm{X}_2)\,(\mathrm{K}_1\mathrm{sh}my\mathrm{ch}n - \mathrm{K}_2\mathrm{sh}ny\mathrm{ch}m)\right]$$

$$+ \sum_{s''} \frac{4\mathrm{R}re^{st}}{s\mathrm{X}(1+r)^2Z''}\left\{\frac{\mathrm{X}+s\mathrm{X}_1}{\mathrm{R}}\alpha\,(n\mathrm{ch}my\mathrm{sh}n - m\mathrm{ch}ny\mathrm{sh}m)\right.$$

$$\left. - r\,(\alpha\mathrm{X}+s\mathrm{X}_2)\,(\mathrm{K}_1\mathrm{ch}my\mathrm{sh}n - \mathrm{K}_2\mathrm{ch}ny\mathrm{sh}m)\right\}, \tag{2.36}$$

$$e = \sum_{s'} \frac{4\mathrm{P}\alpha e^{st}}{s\mathrm{R}\,(1+r)^2Z'}\left\{\frac{\beta-\alpha}{s} + \frac{\mathrm{R}}{\mathrm{M}^2}\frac{(\mathrm{X}+s\mathrm{X}_1)}{\mathrm{X}}\right\}(n^2\mathrm{sh}n\mathrm{ch}my$$

$$- m^2\mathrm{ch}m\mathrm{sh}ny) - \sum_{s'} \frac{4\mathrm{P}e^{st}}{s\mathrm{X}\mathrm{M}^2(1+r)^2Z'}(\mathrm{X}+s\mathrm{X}_2)$$

$$\times\,\{(\alpha^2\mathrm{M}^2+s\mathrm{R}-m^2)\,\mathrm{ch}n\mathrm{ch}my - (\alpha^2\mathrm{M}^2+s\mathrm{R}-n^2)\,\mathrm{ch}m\mathrm{ch}ny\}$$

$$+ \sum_{s''} \frac{4e^{st}}{(1+r)^2Z''}\left[-r^2\,(\mathrm{sh}n\mathrm{sh}my - \mathrm{sh}m\mathrm{sh}ny) + \frac{\mathrm{X}_2}{\mathrm{RX}}\right.$$

$$\times\,\{(\alpha^2\mathrm{M}^2+s\mathrm{R}-m^2)\,\mathrm{sh}n\mathrm{sh}my - (\alpha^2\mathrm{M}^2+s\mathrm{R}-n^2)\,\mathrm{sh}m\mathrm{sh}ny\}$$

$$\left.- \frac{\alpha\mathrm{X}_1}{\mathrm{RX}}\,(n^2\mathrm{sh}n\mathrm{sh}my - m^2\mathrm{sh}m\mathrm{sh}ny)\right], \tag{2.37}$$

where Z' and Z'' are defined by (4.37, 4.38) of Part I.

The values $u_{\text{stat.}}$ and $h_{\text{stat.}}$ in (2.35, 2.36) which correspond to stationary conditions are calculated as residues for $s = o$ and are determined by the formulas

$$u_{\text{stat.}} = \frac{\beta\mathrm{PR}}{\alpha^2\mathrm{M}^2\mathrm{ch}\alpha\mathrm{M}}(\mathrm{ch}\alpha\mathrm{M} - \mathrm{ch}\alpha\mathrm{M}y) + \frac{\mathrm{sh}\alpha\mathrm{M}y}{\mathrm{sh}\alpha\mathrm{M}}, \tag{2.38}$$

$$h_{\text{stat.}} = \frac{\beta\mathrm{PRR}_m}{\alpha^2\mathrm{M}^3\mathrm{ch}\alpha\mathrm{M}}(\mathrm{sh}\alpha\mathrm{M}y - \alpha\mathrm{M}y\mathrm{ch}\alpha\mathrm{M})$$

$$+ \frac{\mathrm{R}_m\,(\mathrm{sh}\alpha\mathrm{M} - \alpha\mathrm{M}\mathrm{ch}\alpha\mathrm{M}y)}{\alpha\mathrm{M}^2\mathrm{sh}\alpha\mathrm{M}}, \tag{2.39}$$

3. CONCLUSIONS

From the solution it is clear that for small values of R, the transition is more rapid as compared to that for large values of R. The shape of the velocity profile does not change in transition state and the large part of the transition occurs in a small time. If the magnetic field is strong, the change is again rapid than otherwise. Again several of the first non-stationary terms in the solutions (2.19–2.21) and (2.35–2.37) represent damped oscillations for a given relation between the parameters. As $t \to \infty$, the flow is determined by the stationary conditions $u_{\text{stat.}}$, $h_{\text{stat.}}$ and $e_{\text{stat.}}$

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CAUSES OF ARIDITY AND INVERSION OVER THE DESERT AREAS OF WEST PAKISTAN AND NEIGHBOURHOOD DURING THE SOUTH-WEST MONSOON SEASON

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Abstract

Views of Flohn (1965, 1966) and of Ramage (1966) regarding the causes of aridity and inversion over the desert areas of West Pakistan and neighbourhood have been examined. It is shown on the basis of climatic features of the area that the inversion is due to air masses and *not* due to subsidence; the aridity of the region is due to absence usually of a mechanism which can break up the inversion and *not* due to the restricted depth of the moist current.

Introduction

It has hitherto been considered that the inversion over West Pakistan during the monsoon season is due to different air masses, deflected trades or moist monsoon air in the lower levels and warmer drier air from Baluchistan plateau side above (Desai, 1966—1, 2; 1967—1, 2); the aridity of the desert area has been taken as being due to inability of the convective clouds to penetrate the inversion.

Flohn (1965, 1966) has expressed the view that the aridity of the desert region is due to subsidence caused by divergence. Ramage (1966) has stated that the inversion over the desert area is due to large-scale subsidence which restricts the depth of the moist current and is responsible for scanty rainfall over that area.

It is proposed to examine in this paper the various facts of observations over the area with a view to decide which of the two causes—air masses considered valid upto 1963 or subsidence (Flohn and Ramage) is responsible for the inversion between about 1·0 and 2·0 km. and scanty rainfall over the desert area of West Pakistan and neighbourhood.

DISCUSSION

Climatic features.—It has been found on analysis of aeroplane ascents over Karachi (Hariharan, 1932) that during a typical monsoon month like July, an inversion usually occurs over Karachi at a height of about 1·0 km. and it is about 500 meter thick, the rise in temperature in the inversion being about 4° C. on an average. The lapse rate below the inversion was adiabatic and above it in the dry air about 6 to 8° C. per km. The winds over Karachi are moderate to strong and mainly from west upto 1·0 km., veer with height and at 3·0 km. are light to moderate between north and east, being somewhat stronger but from about the same direction at 6·0 km. Light rain occurs at times in the mornings from the stratiform clouds below the inversion, but the clouds dissipate as the insolation effect increases. It is also noticed that when above about 3·0 km. the north-easterly to easterly air is a continuation of the moist air from the east, the humidity increases (Hariharan, 1932; Mal and Desai, 1938; Desai and Mal, 1940), the convergence zone between the dry continental air (west to north-west veered to north-east) and the moist easterly air being also over the area.

View-point of Flohn.—Flohn (1965) has considered that the aridity of the desert region is due to the monsoon current becoming divergent as a result of the heat-low over West Pakistan and, therefore, subject to large-scale subsidence, reducing the vertical extent of the moist layer to about 1·5 to 2·0 km. In his comments on Desai's paper (1966—2) Flohn (1966) has also stated that average vertical wind components at altitudes of 1·5 and 2·1 km. computed on the basis of low-level mass divergence, were evidently strongly correlated with the average rainfall map. The following remarks might be made regarding Flohn's conclusions:

(*a*) While there will be divergence of the monsoon current under the influence of the heat-low resulting into subsidence, this effect will decrease with height as it (heat-low) is shallow (Ramage, 1966). Further, as a result of insolation vertical currents would be set up and these will considerably decrease the subsidence effect if not completely obliterate it in the lower levels upto about 2·0 km. if not more. The inversion occurs only between about 1·0 and 2·0 km. This would also show little effect of subsidence in the moist layer, *i.e.*, below about 1·0 km. Computation of the divergence of the mean resultant winds at standard pressure levels over the eastern portion of the heat-low over Indo-Pakistan border area by Bellamy (1949) indicated net ascent below 700 mb. associated with the heat-low circulation and net descent above 700 mb. associated with the convergent easterlies (Ramage, 1966). Thus the computations of Flohn would not appear to be supported by those of Bellamy for levels below 700 mb.

(*b*) The depth of the monsoon current (deflected trades) over the Arabian Sea to the west of about 68° E. is also only about 1·0 to 1·5 km. as over the desert area. It cannot be more than 1·0 to 1·5 km. over the desert area because the current extends north-eastwards from the equator (west of about 60° E. where it is deepest about 2·0 to 3·0 km. according to Fig. 2 of Ramage, 1966) as a wedge below the warmer and drier continental air.

(*c*) The inversion generally disappears only when the upper drier air is replaced by easterly moist air (Hariharan, 1932; Mal and Desai, 1938; Desai and Mal, 1940). As the south-westerly to westerly moist current persists in the lower levels and so also the heat-low, it can be assumed that the inversion between 1·0 and 2·0 km. is due to air masses and not due to subsidence as a result of divergence.

Under the circumstances one is justified to consider that the inversion over the desert area is due to hot air from Baluchistan plateau spreading over the cooler moist air.

View-point of Ramage.—(*a*) Desai (1967—1) has given the mean wind at different levels at Karachi and discussed the weather conditions during August 1963, the period of temperature and humidity data given in Fig. 4 of the paper of Ramage (1966). The Karachi data during August 1963 were generally similar to average monsoon conditions. Humidity increase from 41% at 700 mb. to 75% at 500 mb. would appear to be associated with the close proximity of the boundary between the continental and moist north-easterlies to easterlies. The high humidity at 500 mb. during August 1963 would thus not appear to be due to subsidence of warm moist air from the rain systems from the east and south (Desai, 1967—1).

(*b*) Ramage (1966) has stated that descending motion is generally above 700 mb. and ascending motion below that level. As the inversion is only between about 900 and 825 mb., it cannot be considered as being due to subsidence. The ascending motion below 700 mb. would not appear to be sufficiently strong as the inversion between 1·0 and 2·0 km. is not destroyed.

(*c*) Regarding the temperature differences of 2–6° C. in the middle and upper troposphere between monsoon rain (30–6–1964, 12 GMT) and monsoon lull (15–7–1964, 12 GMT) situations studied by Dixit and Jones

(1964) and referred to by Ramage (1966), the following differences worked out from temperatures obtained from the Met. Office, Poona, are significant:

Temperature differences in ° *C.—Temperature of* 30–6–1964 minus *Temperature of* 15–7–1964

Station / Level mb.	Bombay	Ahmedabad	Jodhpur	New Delhi	Srinagar
500	+5·0 (+1·0)	+0·7	+4·6 (+3·6)	−0·4 (+0·6)	+6·6
300	+9·8 (+3·0)	+6·9	+1·4 (+4·7)	.. (+3·3)	+4·4
200	+2·9 (+0·9)	+8·4	+5·8 (+5·8)	.. (+1·7)	+4·9

The values in bracket are taken from Fig. 16 of Dixit and Jones' paper. They have not considered data for Ahmedabad and Srinagar and given values for New Delhi for 300 and 200 mb. for which data are not complete. Further, even where they have given values, they are different in all the cases except for Jodhpur for 200 mb. where they are the same. From the above table it would appear that the highest difference was at Srinagar at 500 mb., at Bombay at 300 mb. and at Ahmedabad at 200 mb. Thus one does not find highest differences at any level at Jodhpur near the area of heat-low. Ramage would not, therefore, appear justified in using Dixit and Jones' Fig. 16 to support his hypothesis about subsidence in the middle and upper troposphere over the heat-low over West Pakistan.

CONCLUDING REMARKS

From the foregoing discussion it would appear that the views of Flohn regarding low-level divergence giving rise to subsidence and of Ramage regarding subsidence over the heat-low above 700 mb. level cannot explain presence of the inversion between about 1·0 and 2·0 km. over the desert area. While Flohn considers subsidence due to divergence taking place in the lower levels, Ramage considers that there is net ascent below about 700 mb. There is also no question of the depth of the moist layer being restricted to 1·0 to 1·5 km. due to subsidence. According to Fig. 2 of Ramage's paper there is inversion even over the east Arabian Sea with base at 2·0 to 3·0 km. near about 70° E. Large depth of moist current (about 6·0 km.) over the west coast without an inversion is not due to absence of subsidence over there, but mostly due to the presence of the Western Ghats across the path of the deflected trades as suggested by Desai (1966—1, 2; 1967, 1—2) in contrast to the Sind–Kutch and West Saurashtra coasts where there is absence of such barriers. Further, the depth of the deflected trades over the desert area and the Arabian Sea west of about 68° E. is only about 1·0 to 1·5 km. as they advance as a wedge north-east to eastwards below warmer and drier continental air. Thus the view hitherto held that the inversion over the desert area is an air mass one and that its persistence is responsible for the aridity of the region would appear to be substantially valid even today.

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NORMAL VIBRATIONS OF N, N-DIMETHYLFORMAMIDE AND N, N-DIMETHYLACETAMIDE

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ABSTRACT

Infrared and Raman frequencies of N, N-dimethylformamide and N, N-dimethylacetamide as recorded by the authors, in the region 3100 cm.$^{-1}$ to 250 cm.$^{-1}$ are given. The normal co-ordinate treatment of these molecules has been carried out using general quadratic force field and the potential energy distribution of the various modes of vibrations have been calculated to study the nature of absorption frequencies arising out of the in-plane vibrations. The assignments made by the authors in the region 3100 cm.$^{-1}$ to 500 cm.$^{-1}$ are compared with those of Lumley Jones who assigned the frequencies on the basis of band contour studies. These calculations have enabled the authors also to assign the frequencies in the region 500 cm.$^{-1}$ to 250 cm.$^{-1}$ to the various bending modes of vibrations. The C—N stretching frequency in tertiary amides is considerably different from that in primary and secondary amides.

I. INTRODUCTION

SPECTROSCOPIC studies of primary and secondary amides and the normal co-ordinate treatment of these molecules received considerable attention in recent times. Several authors[1–11] have studied the infrared spectra of primary amides like formamide, and acetamide and secondary amides like N-methylformamide and N-methylacetamide and of their deuterated species in various states of aggregation to investigate the nature of intermolecular associations in these molecules and Miyazawa *et al.*, Suzuki, Puranik and Lalitha Sirdeshmukh and the authors[5–7, 9–11] subjected these molecules to normal co-ordinate treatment in order to understand the nature of the absorption frequencies arising out of different modes of vibrations. The main result that emerges out of these studies is that in primary amides, the amide I, the amide II and the amide III bands are essentially due to ν(C=O), $\delta(NH_2)$ and ν(C—N) vibrations respectively. On the other hand, in secondary amides, while the amide I band is essentially a C=O stretch, the amide II and the amide III bands have been shown to arise out of the combined contribution of δ(NH) and ν(C—N) vibrations. These results have been broadly supported from the spectra of N-methylacetamide and acetanilide obtained by Bradbury and Elliot[12] and Soichi Hayashi[13] who used polarised infrared radiation in these studies. Lumley Jones[14] assigned the vibrational frequencies of some secondary and tertiary amides in the region 3500 cm.$^{-1}$ to 500 cm.$^{-1}$ on the basis of band contour studies of infrared absorption bands and Katon *et al.*[15] recorded the spectra of these compounds in the region 700 cm.$^{-1}$ to 250 cm.$^{-1}$ There is no earlier attempt to investigate the nature of the absorption frequencies arising out of the in-plane vibrations in tertiary amides on the basis of normal co-ordinate treatment. The authors have therefore chosen two simplest molecules of the tertiary amides—N, N-dimethylformamide and N, N-dimethylacetamide and subjected them to normal co-ordinate treatment by using the general quadratic force field.

II. EXPERIMENTAL AND RESULTS

The infrared spectra of N, N-dimethylformamide and N, N-dimethylacetamide in the region 3100 cm.$^{-1}$ to 700 cm.$^{-1}$ have been recorded using Perkin-Elmer Model 21 infrared spectrophotometer with NaCl optics. The spectra of the liquids were recorded using microfilms of unknown thickness and of solutions in CCl_4 with matched cells of 0·1 mm. thickness with NaCl windows. The spectra of the pure amides were also recorded in the region 700 cm.$^{-1}$ to 400 cm.$^{-1}$ with Perkin-Elmer Model 337 grating spectrophotometer, and in the region of 400 cm.$^{-1}$ to 250 cm.$^{-1}$ with Perkin-Elmer Model 521 grating spectrophotometer. The Raman spectra of these substances were recorded with Fuess glass spectrograph and Hilger's Raman source unit and λ 4358 was used as the exciting radiation. The infrared and Raman frequencies, as recorded by the authors and the assignments are given in Tables I and II and the corresponding infrared and Raman spectra are shown in Figs. 1, 2, 3 and 4. The infrared bands at 1256 cm.$^{-1}$ and 1259 cm.$^{-1}$ in the two amides are strong whereas the bands at 865 cm.$^{-1}$ and 738 cm.$^{-1}$ are weak. But in Raman spectra, the frequencies at 866 cm.$^{-1}$ and 743 cm.$^{-1}$ are the strongest lines while the other two frequencies at 1230 cm.$^{-1}$ and 1259 cm.$^{-1}$ are relatively less intense. Similarly the Raman line at 960 cm.$^{-1}$ which is assigned to ν(C—CH$_3$) vibration in N, N-dimethylacetamide is fairly strong whereas the corresponding band in infrared is weak.

TABLE I

Infrared and Raman spectra of N, N-dimethylformamide

(Frequencies in $cm.^{-1}$)

Infrared		Raman	Assignment
Pure amide	Amide in solution of CCl_4	Pure amide	
3000 (w)	..	3006 (2)	ν_{as} (CH_3) N
2950 (m)	2933	2945 (5)	ν_s (CH_3) N
2875 (ms)	2870	2873 (5)	ν (C—H)
..	..	2823 (1)	1664+1160
1685 (vs)	1685	1664 (4)	ν (C=O)
1502 (m)	1499	1442 (6)	ν (C—N)
1443 (m)	1435	..	δ_{as} (CH_3) N
1404 (m)	1404	1407 (6)	δ_s (CH_3) N
1393 (s)	1381	..	δ (C—H)
1256 (ms)	1256	1230 (3)	ν_{as} (N—CH_3)
1149 (vw)	1149	1160 (2 *b*)	ω (CH_3) N
1091 (vs)	1087	1094 (4 *b*)	γ (CH_3) N
1064 (w)	1064	..	δ (C—H) $\perp$
865 (w)	865	866 (6)	ν_s (N—CH_3)
662 (s)	..	667 (6)	δ (O=C—N)
400 (w)	..	405 (4)	δ (CH_3—N—CH_3)
355 (m)	..	354 (4)	τ (C—N)
320 (w)	..	316 (3)	γ (CH_3—N—CH_3)

TABLE II

Infrared and Raman spectra of N, N-dimethylacetamide

(Frequencies in cm.$^{-1}$)

Infrared		Raman	Assignment
Pure amide	Amide in solution of CCl$_4$	Pure amide	
3003 (m)	3020	3050 (3)	ν_{as} (CH$_3$) N
2941 (ms)	2959	2929 (6)	ν_s (CH$_3$) N
2870 (w.sh)	..	2868 (4)	ν_{as} (CH$_3$) C
2820 (w.sh)	..	2827 (7)	ν_s (CH$_3$) C
1653 (vs)	1657	1646 (6)	ν (C=O)
1494 (m)	1494	1452 (5)	ν (C—N)
1440 (m)	1440	..	δ_{as} (CH$_3$) C, N
1395 (5)	1395	1412 (5)	δ_s (CH$_3$) N
1351 (m)	1351	1359 (2)	δ_s (CH$_3$) C
1259 (s)	1263	1259 (3)	ν_{as} (N—CH$_3$)
1183 (s)	1185	1182 (3)	ω (CH$_3$) N
1054 (m)	1056	..	ω (CH$_3$) C
1029 (m)	1029	..	r (CH$_3$) N
1013 (s)	1013	1016 (2)	r (CH$_3$) C
957 (w)	957	960 (4)	ν (C—CH$_3$)
738 (w)	..	743 (7)	ν_s (N—CH$_3$)
593 (s)	..	591 (4)	δ (O=C—N)
476 (m)	..	470 (2)	δ (CH$_3$—N—CH$_3$)
422 (m)	..	422 (3)	r (C—CH$_3$)
..	..	262 (2)	r (CH$_3$—N—CH$_3$)

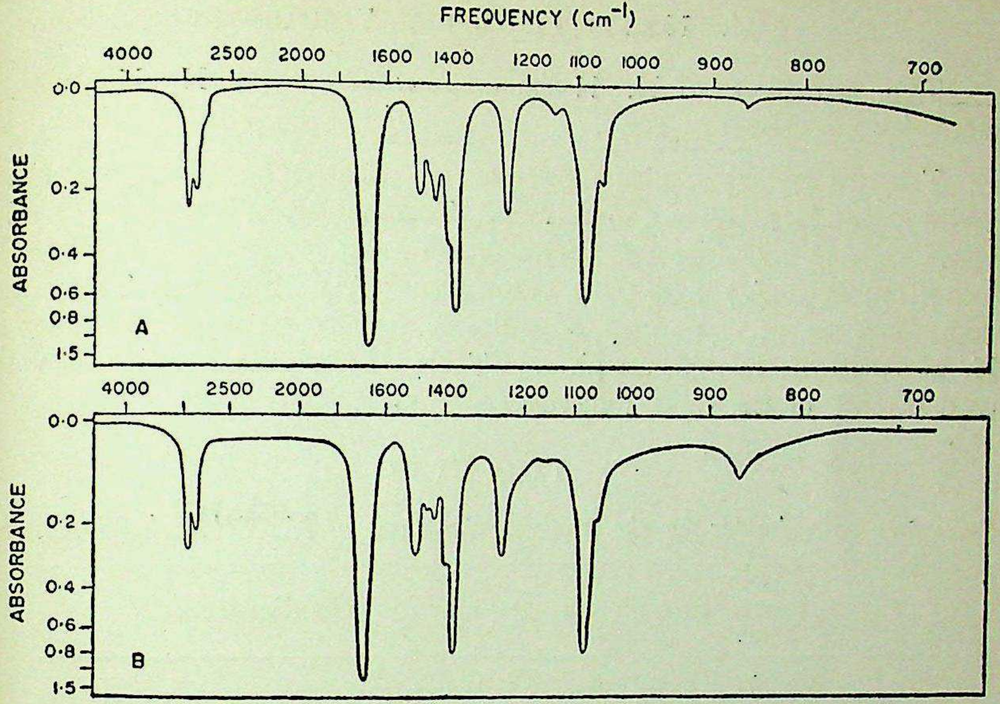


FIG. 1. Infrared spectra of (A) Dimethylformamide, (B) Dimethylformamide in carbon tetra-chloride.

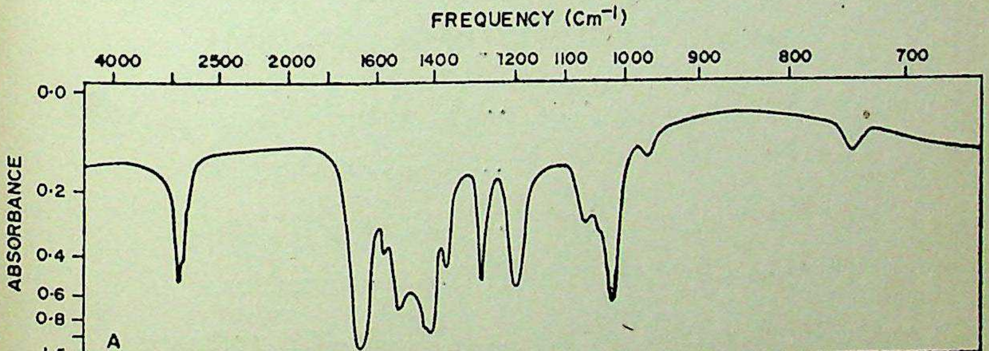


FIG. 2. Infrared spectra of (A) Dimethylacetamide, (B) Dimethylacetamide in carbon tetra-chloride.

III. NORMAL CO-ORDINATE TREATMENT

The structures of N, N-dimethylformamide and N, N-dimethylacetamide are shown in Fig. 5.

The two tertiary amide molecules are treated as six-body problems taking each CH_3 group as a point mass. These molecules belong to the point group C_s and therefore the twelve fundamental frequencies are classified into 9 in-plane (A′) and three out-of-plane (A″) vibrations. The orthonormalised set of symmetry co-ordinates for the in-plane vibrations of N, N-dimethylformamide are given in Table III and similar expressions are used in case of the other molecule.

TABLE III

Symmetry co-ordinates for the in-plane vibrations of N, N-dimethylformamide

Symmetry co-ordinates	Vibrational mode
$R_1 = 1/\sqrt{2}\,(\triangle d - \triangle e)$	.. N—CH_3 asymmetric stretching
$R_2 = 1/\sqrt{2}\,(\triangle d + \triangle e)$	.. N—CH_3 symmetric stretching
$R_3 = \triangle c$	.. C—H stretching
$R_4 = \triangle b$	.. C=O stretching
$R_5 = \triangle a$	.. C—N stretching
$R_6 = 1/\sqrt{6}\,(2\triangle de - \triangle ad - \triangle ae)$	.. CH_3—N—CH_3 bending
$R_7 = 1/\sqrt{2}\,(\triangle ac - \triangle bc)$	.. C—H deformation
$R_8 = 1/\sqrt{2}\,(\triangle ad - \triangle ae)$	.. CH_3—N—CH_3 rocking
$R_9 = 1/\sqrt{6}\,(2\triangle ab - \triangle ac - \triangle bc)$	.. O=C—N bending
$R_{10} = 1/\sqrt{3}\,(\triangle ad + \triangle ae + \triangle de)$	.. Redundant
$R_{11} = 1/\sqrt{3}\,(\triangle ac + \triangle bc + \triangle ab)$	.. Redundant

The elements of the F-matrix have been obtained from the expression

$$F = U f \tilde{U} \qquad (1)$$

using general quadratic potential energy matrix containing the valence forces and their interactions. The elements of the G-matrix have been derived using Decius tables.[16] The structure parameters used in these calculations are given in Table IV.

TABLE IV

Structure parameters

N, N-Dimethylformamide		N, N-Dimethylacetamide	
Bond distances	Inter-bond angles	Bond distances	Inter-bond angles
$r(\mathrm{C{=}O}) = 1{\cdot}23$ Å	$\mathrm{O{=}C{-}N} = 120°$	$r(\mathrm{C{=}O}) = 1{\cdot}23$ Å	$\mathrm{O{=}C{-}N} = 123°$
$r(\mathrm{C{-}N}) = 1{\cdot}29$ Å	$\mathrm{N{-}C{-}H} = 120°$	$r(\mathrm{C{-}N}) = 1{\cdot}29$ Å	$\mathrm{N{-}C{-}CH_3} = 117°$
$r(\mathrm{C{-}H}) = 1{\cdot}07$ Å	$\mathrm{H{-}C{=}O} = 120°$	$r(\mathrm{C{-}C}) = 1{\cdot}55$ Å	$\mathrm{CH_3{-}C{=}O} = 120°$
$r(\mathrm{N{-}C}) = 1{\cdot}47$ Å	$\mathrm{C{-}N{-}CH_3} = 120°$	$r(\mathrm{N{-}C}) = 1{\cdot}47$ Å	$\mathrm{C{-}N{-}CH_3} = 120°$
..	$\mathrm{CH_3{-}N{-}CH_3} = 120°$	..	$\mathrm{CH_3{-}N{-}CH_3} = 120°$

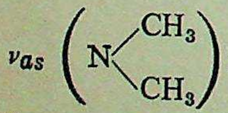
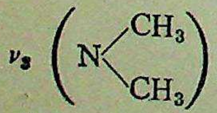
The calculations of normal vibrations of these tertiary amide molecules were made by the method of Wilson.[17,18] For the solution of the secular determinant which has the dimensionality of nine by nine, a programme was written in Fortran language on the basis of the modified Danielewsky's method[19] for Model 2, IBM, 1620 digital computer to compute the polynomial coefficients. IBM 1620 general programme library file No. 7.0.032 was used to extract the roots of the polynomial. At first the force constants were transferred from allied molecules[7,10] and alterations were made in them to obtain a close fit between the observed and calculated frequencies in case of N, N-dimethylformamide. Of the fifteen force constants, ten force constants were transferred from N, N-dimethylformamide to N, N-dimethylacetamide and only two constants were to be slightly altered to get a close fit between the observed and calculated frequencies. The rest of the five force constants are related to the stretching, bending and interaction constants of the C—H group in N, N-dimethylformamide and these are naturally different from those related to the C—CH$_3$ group in N, N-dimethylacetamide. The final sets of force constants used in the numerical computations are given in Table V.

The stretching force constants of C=O and C—N bonds have intermediate values of the force constants which one expects from the idealised double

TABLE V

Force constants of N, N-dimethylformamide and N, N-dimethylacetamide

Type of force constant	Amide	
	N, N-dimethyl formamide	N, N-dimethyl acetamide
Bond stretching ..	$f_d = f_e = 4\cdot7$	$f_d = f_e = 4\cdot7$
	$f_c = 4\cdot5$	$f_c = 3\cdot0$
	$f_b = 9\cdot0$	$f_b = 9\cdot0$
	$f_a = 6\cdot8$	$f_a = 6\cdot8$
	$f_{ab} = 1\cdot5$	$f_{ab} = 1\cdot5$
	$f_{bc} = 0\cdot9$	$f_{bc} = 0\cdot9$
Bond bending ..	$f_{ca} = 0\cdot54$	$f_{ca} = 0\cdot8$
	$f_{ad} = f_{ae} = 0\cdot80$	$f_{ed} = f_{ae} = 0\cdot9$
	$f_{ed} = 0\cdot85$	$f_{ed} = 1\cdot2$
	$f_e^{d} = 0\cdot1$	$f_e^{d} = 0\cdot1$
Bond/bond ..	$f_a^{b} = 0\cdot8$	$f_a^{b} = 0\cdot8$
	$f_b^{c} = 0\cdot4$	$f_b^{c} = 1\cdot2$
	$f_e^{a} = 1\cdot8$	$f_c^{a} = 1\cdot2$
	$f_c^{ca} = 0\cdot3$	$f_c^{ca} = 0\cdot6$
Bond/angle ..	$f_e^{bc} = 0\cdot9$	$f_c^{bc} = 0\cdot9$

bond and single bond linkages of these atoms, indicating partial double and single bond characters for these linkages in amides. Although the  $\nu_{as}\left(N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$ frequencies are almost the same in both the amides, the frequencies arising out of the  $\nu_s\left(N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}\right)$, $\delta(CH_3{-}N{-}CH_3)$, $\gamma(CH_3{-}N{-}CH_3)$ and $\delta(O{=}C{-}N)$ vibrations are considerably different in the two amides. But the corresponding stretching and bending force constants f_e, f_d, f_a, f_b, f_{ab}, f_{bc} have same values and f_{ad}, f_{ae} and f_{ed} are only slightly different.

IV. POTENTIAL ENERGY DISTRIBUTIONS AND NATURE OF THE ABSORPTION FREQUENCIES

The elements of the L-matrix in case of each molecule have been evaluated by a set of homogeneous equations, represented by

$$(\mathrm{GF} - \mathrm{E}\lambda_k)\, a_k = 0 \tag{2}$$

where a_k is the k-th column of matrix 'a' and the normalisation factor N_k is obtained from

$$\mathrm{N}_k{}^2 \sum_{tt'} \mathrm{F}_{tt'}\, a_{tk}\, a_{t'k} = \lambda_k. \tag{3}$$

The elements of the L-matrix have been obtained by multiplying each column a_k by the corresponding normalisation factor N_k. The elements of the L-matrices are thus normalised to $\mathrm{L}\tilde{\mathrm{L}} = \mathrm{G}$. Using the expression $(\mathrm{F}_{ii}\mathrm{L}_{is}{}^2/\lambda_s) \times 100$, the potential energy distribution of each normal mode among the various symmetry co-ordinates is calculated and given in Tables VI and VII.

TABLE VI

The observed and calculated frequencies and potential energy distribution of different normal modes of vibrations of N, N-dimethylformamide

Mode of vibration	Frequency		P.E.D.								
	Obser.	Cal.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
ν_{as} (CH_3—N—CH_3) ..	1256	1252	48	10	2	18	14	4	0	4	1
ν_s (CH_3—N—CH_3) ..	865	888	23	35	0	5	3	4	4	0	29
ν (C—H) ..	2870	2882	0	0	90	1	0	0	2	0	0
ν (C=O) ..	1685	1704	3	0	12	45	8	0	41	4	4
ν (C—N) ..	1499	1510	11	3	16	3	32	1	16	6	36
δ_{as} (CH_3—N—CH_3) ..	400	418	2	2	1	1	9	85	0	1	1
δ (C—H) ..	1381	1345	3	8	0	25	27	3	46	0	0
δ_s (CH_3—N—CH_3) ..	320	304	3	0	0	0	2	5	0	75	13
δ (O=C—N) ..	662	661	8	41	2	5	20	5	0	2	18

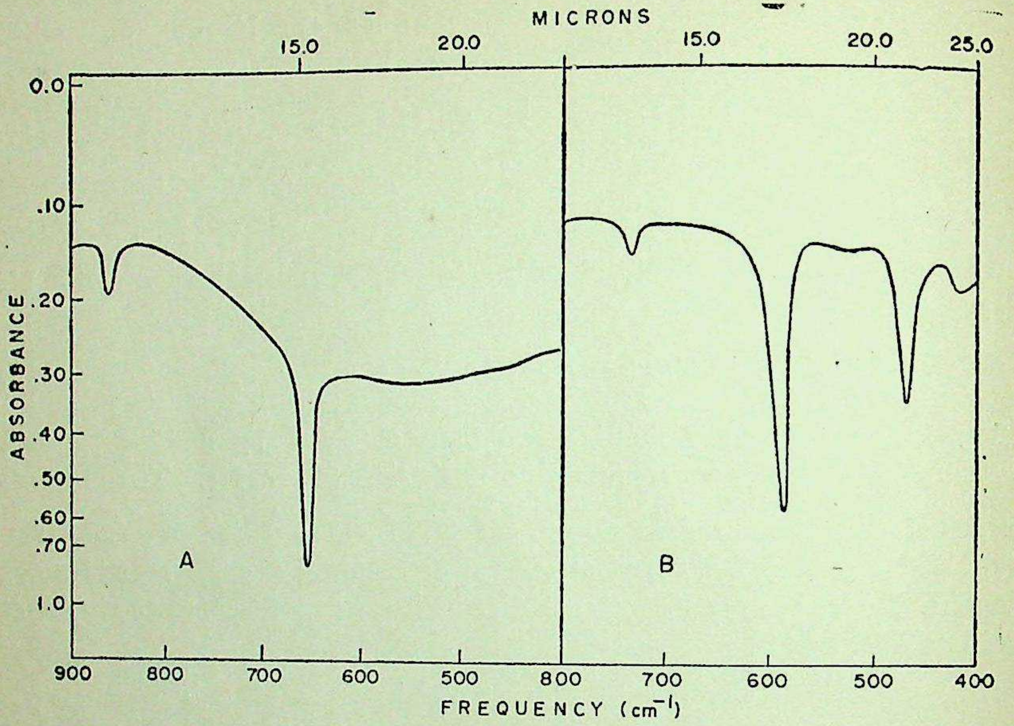


FIG. 3. Infrared spectra of (A) Dimethylformamide, (B) Dimethylacetamide.

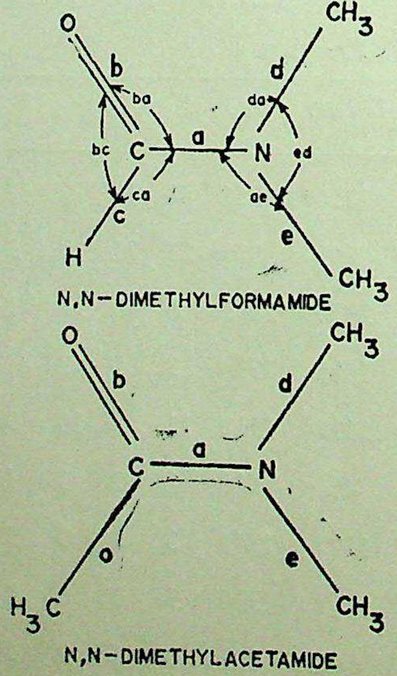

O
CH3
b
d
ba
da
bc
C
a
N
ed
ca
ae
c
e
H
CH3
N,N-DIMETHYLFORMAMIDE
O
CH3
b
d
C
a
N
o
e
H3C
CH3
N,N-DIMETHYLACETAMIDE

FIG. 5. Structures of Dimethylformamide and Dimethylacetamide.

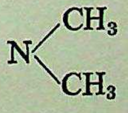
TABLE VII

The observed and calculated frequencies and potential energy distribution of different normal modes of vibrations of N, N-dimethylacetamide

Mode of vibration	Frequency		P.E.D.								
	Obser.	Cal.	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	R_9
ν_{as} (CH_3—N—CH_3) ..	1263	1254	37	12	1	28	11	6	0	3	1
ν_s (CH_3—N—CH_3) ..	738	726	2	40	29	4	5	0	5	2	2
ν (C—CH_3) ..	957	986	26	21	26	0	2	6	4	0	34
ν (C=O) ..	1657	1662	3	1	2	63	21	1	6	5	7
ν (C—N) ..	1494	1504	17	5	5	0	39	4	1	8	35
δ_{as} (CH_3—N—CH_3) ..	476	503	8	3	18	9	5	37	20	9	2
γ (C—CH_3) ..	422	381	2	0	3	1	12	32	29	16	5
δ_s (CH_3—N—CH_3) ..	262	258	1	4	0	0	1	0	32	56	10
δ (O=C—N) ..	593	605	3	17	40	0	11	14	4	0	10

Tables VI and VII also give the observed and calculated frequencies.

The bands at 1256 cm.$^{-1}$ and 865 cm.$^{-1}$ in dimethylformamide or at 1263 cm.$^{-1}$ and 738 cm.$^{-1}$ in dimethylacetamide are due to the asymmetric and symmetric stretching vibrations of the



$N(CH_3)_2$

group. In both the molecules, to the asymmetric stretching frequency of the N—$(CH_3)_2$ group, contribution comes from the symmetric stretch of the same group and also from ν (C=O) and ν (C—N) vibrations. On the other hand, to the symmetric stretching vibration of the N—$(CH_3)_2$ in dimethylformamide, a considerable contribution is from the asymmetric stretching vibration of the same group, but in dimethylacetamide ν (C—CH_3) vibration makes substantial contribution to this absorption. This may explain for the difference in the symmetric stretching frequencies of the N—$(CH_3)_2$ group in these two molecules.

The band at 2870 cm.$^{-1}$ in dimethylformamide is due to the ν(C—H) vibration and the potential energy distribution shows that the contribution of other modes to this one is almost negligible. Such results are characteristic of stretching vibrations of C—H and N—H linkages.[5,6] The corresponding stretching vibration in dimethylacetamide is the ν(C—CH_3) vibration at 957 cm.$^{-1}$ The contributions from the N—CH_3 stretching and OCN bending vibrations to this mode are considerable.

The band at 1657 cm.$^{-1}$ in dimethylacetamide or at 1685 cm.$^{-1}$ in dimethylformamide is essentially due to the C$'$=O stretching vibration. To the band at 1657 cm.$^{-1}$ in dimethylacetamide, there is a considerable contribution from C—N stretch and this result is similar to that of Suzuki[6] in case of acetamide. But in dimethylformamide, to the C=O stretch at 1685 cm.$^{-1}$, a substantial contribution is from δ(CH) vibration and the contribution from C—N stretch is relatively low. The normal co-ordinate treatment of formamide molecule by Suzuki[5] also shows that the δ(CH) vibration contributes substantially to ν(C=O) apart from the ν(C—N) vibration.

The normal co-ordinate treatment of primary amide molecules[5,6] shows that the band in the region of 1350 cm.$^{-1}$ to 1300 cm.$^{-1}$ is the C—N stretch. In secondary amides,[9] the bands in the regions of 1550 cm.$^{-1}$ and 1300 cm.$^{-1}$ to 1250 cm.$^{-1}$ are assigned as due to the combined contribution of δ(NH) and ν(C—N) vibrations. But a band in the region of 1500 cm.$^{-1}$ is assigned to C—N stretching vibration in tertiary amides and the potential energy distribution supports this assignment. This result is strikingly different from that in primary and secondary amides and is in agreement with the assignment of Lumley Jones made on the basis of band contour studies of infrared absorption bands.

The band at 1381 in dimethylformamide is due to δ(CH) vibration and the C=O and the C—N stretches contribute to this frequency. It is of interest to note from the potential energy distribution that the deformation CH vibration, likewise contributes to the C=O and the C—N stretches. The bands at 405 cm.$^{-1}$ and 316 cm.$^{-1}$ in dimethylformamide are due to the bending and rocking modes of vibrations of N—$(CH_3)_2$ group and the contributions of other modes to these two bands are small. But in dimethylacetamide, the bands at 476 cm.$^{-1}$, 262 cm.$^{-1}$ and 422 cm.$^{-1}$ are assigned to the bending, rocking vibrations of N—$(CH_3)_2$ group and the rocking vibration of C—CH_3 group respectively and the potential distributions indicate considerable interaction between these three modes of vibrations. This may explain for the difference in the bending frequencies of N—$(CH_3)_2$ group in dimethylformamide and dimethylacetamide.

It has already been mentioned that Lumley Jones assigned the frequencies in the region 3100 cm.$^{-1}$ to 500 cm.$^{-1}$ on the basis of band contour studies. The assignments made by the authors of the in-plane vibrational frequencies in the same region on the basis of the normal co-ordinate treatment are in agreement with those of Lumley Jones. In addition, the normal vibrational studies enabled the authors to study the nature of each absorption band and assign the low frequencies in the region 500 cm.$^{-1}$ to 250 cm.$^{-1}$ for the first time to the various bending modes of vibrations.

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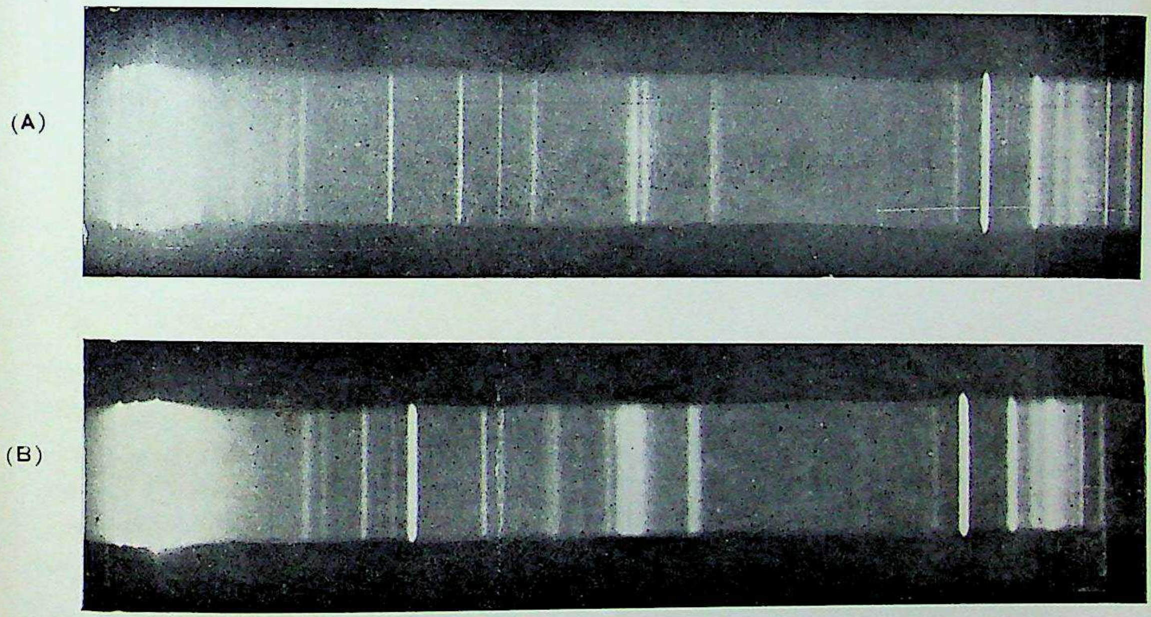

FIG. 4. Raman spectra of (A) Dimethylformamide, (B) Dimethylacetamide.

A POLAROGRAPHIC STUDY OF MERCURIC CYANIDE COMPLEXES WITH ALKALI HALIDES

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Abstract

A polarographic study of the complexation reactions between mercuric cyanide and alkali halides has been carried out. In basic solutions, the existence of two species $Hg(CN)_2X^-$ and $Hg(CN)_3X^{--}$ being reduced has been concluded (where X = Cl, Br or CNS). The cyanide released by the reduction combines with $Hg(CN)_2X^-$ at or around the surface of the drop to form $Hg(CN)_3X^{--}$. The logarithms of the overall formation constants of these species at an ionic strength of 2·0 are: 36·19 and 39·43 for chloride, 35·99 and 39·10 for bromide and 36·30 and 38·74 for thiocyanate complexes.

Introduction

The complexation reactions between mercuric cyanide and alkali halides have been a subject of recent interest. Bourion and Rouyer[3] were the first to report the existence of complex ion $Hg(CN)_2Cl^-$ from an ebullioscopic study. Penneman and Jones[5] employing infra-red absorption techniques have shown the existence of two complexes, *i.e.*, $Hg(CN)_2Cl^-$ and $Hg(CN)_3Cl^{--}$ between mercuric cyanide and chloride ions. With the polarographic data available in literature on the study of mercuric cyanide and its complexes in different pH regions, it was of interest to study in detail the complex formation between mercuric cyanide and alkali halides polarographically.

The polarography of mercuric cyanide has been extensively studied by Tomes,[7] by Newman, Cabral and Hume[4] and by Tanaka and Murayama.[6] These workers have explained the behaviour of mercuric cyanide in different pH regions and found evidence for the presence of three complexes: $Hg(CN)_2$, $Hg(CN)_3^-$ and $Hg(CN)_4^{--}$. The stability constants of these have also been computed from the polarographic data. As the $E_{\frac{1}{2}}$ of mercuric cyanide was found not to be concentration independent, a concentration independent term E_f which is related to E_{de} by the following equation was derived:

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$$E_{de} = E_f + 0{\cdot}030 \log \frac{i_d - i}{i^2}$$

where

$$E_f = E' + 0{\cdot}060 \log \frac{K_A + C_H{}^{\circ} + fH^+ + fCN^-}{K_A}$$

in which

$$E' = E_0 + 0{\cdot}030 \log \frac{d_I{}^2}{d_n K_2 f^2 CN^-}$$

where K_A is the ionization constant of hydrogen cyanide, $C_H{}^{\circ}$ is the concentration of hydrogen ion at the electrode surface, f_H and f_{CN^-} are activity coefficients, E_0 is the standard potential of the mercury—mercuric ion couple, d_I and d_n are the diffusion coefficients of cyanide and mercuric cyanide respectively, and K_2 the formation constant of mercuric cyanide. If all measurements are done at a constant high ionic strength, activity coefficients may be assumed to be constant. The above derivation has also been utilised by Newman and Hume[8] for the study of the equilibria $Hg(CN)_3^- + X^- = Hg(CN)_3X^{--}$ and calculating the formation constants of the species $Hg(CN)_3X^{--}$ where $X = Cl$, Br or CNS.

EXPERIMENTAL

Reagents.—Mercuric cyanide (E. Merck) was recrystallised from conductivity water before being used. For all other chemicals, analytical grade reagents were used. All solutions were de-aerated with purified nitrogen.

Apparatus.—A home-made polarograph was used. The capillary had a drop time of 1-8 secs. and a flow of 8·010 mg/sec. pH measurements of all solutions were carried out with a Cambridge bench-type pH-meter.

Techniques and Conditions.—For all polarographic experiments, the ionic strength was maintained at 2·0 M with sodium nitrate and 0·02% gelatin was used as maximum supressor. The reference electrode was the conventional saturated calomel, connected to the cell by a saturated potassium nitrate agar bridge. The solutions were freed of dissolved oxygen by passing nitrogen through them for 15 minutes. Residual currents were taken for each solution. The blanks contained everything except the electro-active material.

CALCULATIONS AND RESULTS

Polarograms were run with solutions containing a known concentration of mercuric cyanide and an excess of alkali halide solution maintaining a constant high ionic strength of 2. In such a solution the possible species given by Newman and Hume are $Hg(CN)_2X^-$ and $Hg(CN)_2X_2^{=}$ but the only species existing would be $Hg(CN)_2X^-$. This has been confirmed by the infra-red studies of Penneman and Jones[5] and our preparative studies.[1, 2] The other possibility is $Hg(CN)_3X^{--}$ which can exist only when the concentration of mercuric cyanide is more and the cyanide ions liberated as a result of the electrode reaction:

$$Hg(CN)_2X^- + 2e^- \longrightarrow Hg + 2CN^- + X^-$$

combine with $Hg(CN)_2X^-$. Another possibility is $Hg(CN)_3^-$ which cannot exist as the predominating species at low concentrations at which we have assumed the existence of $Hg(CN)_2X^-$ because of lesser chances of the availability of CN^- ions and high alkali halide/$Hg(CN)_2$ ratio whereas at higher concentrations in presence of excess alkali halide it will exist as $Hg(CN)_3X^{--}$ the overall constants of $Hg(CN)_3X^{--}$ being higher.

In our studies, the low pH regions (1–5·5) was not used because of reported irreversibility[4] of the electrode reaction. However, a few polarograms were run in the region 5·5–9·5 but they gave slopes (S) greater than 30 mvs., when a plot of E_{de} was taken against even

$$\log \frac{i_d - i}{i^3} \text{ and } \log \frac{i_d - i}{i^4}.$$

Further, the S and E_f values did not show any regular change. The data are given in Table I. This may be attributed to complex formation and residual irreversibility which appears to have become pronounced in the case of mixed solutions of mercuric cyanide and alkali halides Therefore, the basic region was studied in greater detail. In basic region E_f is independent of pH. As the number of complexing ions in $Hg(CN)_2X^-$ like $Hg(CN)_3^-$ is 3, plots of E_{de} *vs.* $\log i_d - i/i^3$ were taken for different concentrations of mercuric cyanide. It was found that as the concentration of mercuric cyanide

TABLE I

Hg $(CN)_2$ in mM	pH	KCl 100 mM					
		Characteristics from					
		E_{dc} *vs.* log $i_d - i/i^2$ in mvs.		E_{de} *vs.* log $i_d - i/i^3$		E_{dc} *vs.* log $i_d - i/i^4$	
		S	$-E_f$	S	$-E_f$	S	$-E_f$
0·50	5·70	42	324	34	318	30	312
1·00	5·72	58	312	42	296	36	284
1·50	5·65	72	332	58	302	48	276
2·00	5·60	66	314	52	288	44	246
1·00	7·22	48	260	44	232	36	220
2·00	7·20	76	258	64	210	52	192

increases the slope increases (ranging between 32 mvs.–44 mvs.) and E_f decreases. Consequently, due to possible existence of $Hg(CN)_3X^{--}$ having 4 attached groups like $Hg(CN)_4^{--}$ at higher concentrations, plots of E_{de} *vs.* log $i_d - i/i^4$ were also taken. The data are summarised in Tables II–IV for chloride, bromide and thiocyanate systems. Values of E_f for different

TABLE II

Hg $(CN)_2$ in mM	pH	KCl 100 mM, NaOH 1 mM					
		Characteristics from E_{dc} *vs* log $i_d - i/i^3$ in mvs.		Characteristics from E_{dc} *vs.* log $i_d - i/i^4$		i_d (μa)	$d_{comp.} \times 10^{-3}$ (μa/M)
		S	$-E_f$	S	$-E_f$		
0·25	10·12	34	332*	28	332	2·40	9·60
0·50	10·12	34	322	30	312*	4·15	8·30
0·75	10·12	40	306	38	288	6·30	8·40
1·00	10·12	40	300	40	280	8·80	8·80
1·50	10·10	40	296	40	268	12·75	8·50
2·00	10·10	40	292	40	260	17·10	8·55

TABLE III

$Hg(CN)_3$ in mM	pH	KBr 100 mM, Characteristics from E_{de} vs. log $i_d - i/i^3$ in mvs.		NaOH 1 mM Characteristics from E_{de} vs. log $i_d - i/i^4$		i_d (μa)	$d_{comp.} \times 10^{-3}$ (μa/M)
		S	$-E_f$	S	$-E_f$		
0·25	9·96	32	324*	26	324*	2·05	8·20
0·50	9·94	38	308	28	304	4·45	8·90
0·75	9·94	38	310	30	302*	6·20	8·27
1·00	9·94	40	292	32	280	9·00	9·00
2·00	9·92	44	280	36	266	17·75	8·88

TABLE IV

$Hg(CN)_2$ in mM	pH	KCNS 100 mM, Characteristics from E_{de} vs. log $i_d - i/i^3$ in mvs.		NaOH 1 mM Characteristics from E_{de} vs. log $i_d - i/i^4$		i_d (μa)	$d_{comp.} \times 10^{-3}$ (μa/M)
		S	$-E_f$	S	$-E_f$		
0·25	9·65	30	336*	26	336	2·50	10·00
0·50	9·65	34	312	30	294	4·70	9·48
0·75	9·65	36	298	30	292*	6·60	8·80
1·00	9·62	40	280	34	266	10·90	10·90
2·00	9·60	52	278	40	262	17·50	8·75

* Value of E_f for the particular species.

species, *i.e.*, $Hg(CN)_2X^-$ and $Hg(CN)_3X^{--}$ were obtained from polarograms where the log plots of $i_d - i/i^3$ and $i_d - i/i^4$ respectively gave the best slope nearing 30 mvs. In basic solutions containing complex species:

$$E_f = E_0 - 0\cdot030 \log \frac{d_{comp.} K(X^-) f^n_{CN^-} f_{Cl^-}}{d_I^n \, d_{Cl^-}}$$

where

$E_0 = 612$ mvs. n = cyanide-mercury ratio

$d_{comp.}$ = diffusion coefficient of complex in μa/M

d_1 = diffusion coefficient of cyanide ions in μ_a/M
= $7 \cdot 1 \times 10^3$ (4)

d_{Cl^-} = diffusion coefficient of chloride ions μ_a/M
(neglected, Cl^- being in *xs*)

K = formation constant of complex

(X^-) = concentration of complexing agent

f_{CN^-} and f_{Cl^-} = activity coefficients (taken as unity because of high ionic strength).

From the values of E_f obtained, the values of K for $Hg(CN)_2X^-$ and $Hg(CN)_3X^{--}$ were obtained from the above equation

$$\log K_{Hg(CN)_2Cl^-} = 36 \cdot 19 \quad \log K_{Hg(CN)_2Br^-} = 35 \cdot 99$$

$$\log K_{Hg(CN)_2Cl^-} = 39 \cdot 43 \quad \log K_{Hg(CN)_3Br^-} = 39 \cdot 10$$

$$\log K_{Hg(CN)_2CNS^-} = 36 \cdot 30$$

$$\log K_{Hg(CN)_3CNS^{--}} = 38 \cdot 74$$

Further, in order to confirm the existence of the species $Hg(CN)_3X^{--}$ polarograms with equimolar concentration of mercuric cyanide and potassium cyanide and excess of the alkali halide were run. It was observed that E_{de} *vs.* $\log i_d - i/i^4$ plots gave slopes either 30 mvs. or quite near to it and the half-wave potential obtained from different concentrations varied within 10 mvs. The plots of E_{dc} *vs.* $\log i_d - i/i^3$ gave slopes which were irregular and much above 30 mvs. The results along with log K values for the species $Hg(CN)_3X^{--}$ are summarised in Tables V–VII.

TABLE V

Hg (CN)$_2$ or KCN in mM	pH	KCl 100 mM,		NaOH 1 mM				
		Characteristics from E_{de} *vs.* $\log i_d - i/i^3$ in mvs.		Characteristics from E_{de} *vs.* $\log i_d - i/i^4$		i_d (μ_a)	$d$comp. $\times 10^{-3}$ (μ_a/M)	log K
		S	$-E_f$	S	$-E_f$			
0·25	9·21	40	292	32	294	1·85	7·40	38·88
0·50	9·32	36	304	32	298	4·50	9·00	38·93
0·75	9·45	38	306	32	300	5·75	7·67	39·07
1·00	9·40	40	302	32	292	9·10	9·10	38·73
2·00	9·34	46	296	36	284	17·00	8·50	33·49

TABLE VI

Hg $(CN)_2$ or KCN in mM	pH	KBr 100 mM,				NaOH 1 mM		
		Characteristics from E_{de} *vs.* log $i_d - i/i^3$ in mvs.		Characteristics from E_{de} *vs.* log $i_d - i/i^4$		i_d (μa)	*d*comp. $\times 10^{-3}$ (μa/M)	log K
		S	$-E_f$	S	$-E_f$			
0·25	9·92	36	310	30	310	2·70	10·80	39·25
0·50	9·95	36	314	30	310	5·10	10·20	39·27
0·75	10·02	38	320	32	310	6·80	9·07	39·30
1·00	10·05	40	328	34	308	8·70	8·70	39·27
2·00	9·97	48	320	40	300	16·90	8·45	39·00

TABLE VII

Hg $(CN)_2$ or KCN in mM	pH	KCNS 100 mM,				NaOH 1 mM		
		Characteristics from E_{de} *vs.* log $i_d - i/i^3$ in mvs.		Characteristics from E_{de} *vs.* log $i_d - i/i^4$		i_3 (μa)	*d*comp. $\times 10^{-3}$ (μa/M)	log K
		S	$-E_f$	S	$-E_f$			
0·25	10·07	34	306	32	310	2·45	9·80	39·29
0·50	10·00	40	310	32	302	6·70	13·40	38·87
0·75	10·05	40	300	32	296	9·20	12·27	38·83
1·00	10·07	44	312	36	296	12·00	12·00	38·74

However, as the above differently determined values of stability constants for Hg $(CN)_3X^{--}$ show, no conclusion could be drawn regarding the order of stabilities of the chloride, bromide and thiocyanate complexes because of very small differences in the values of the three species, although the preparative studies have clearly indicated that the chloride complexes are the least stable as also given by Newman and Hume.

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PROPAGATION OF SOUND PULSES IN A HOMOGENEOUS LAYER UNDER AN INHOMOGENEOUS HALF SPACE

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Abstract

We consider the propagation of two-dimensional sound pulses in a homogeneous layer $-y_1 \leqslant y \leqslant 0$. It is bounded by a plane stratified inhomogeneous half space $y \geqslant 0$ on one side and a perfectly reflecting boundary on the other. A line source is situated in the layer. The boundary condition is $\phi = 0$ or $\partial\phi/\partial y = 0$ at $y = -y_1$, where ϕ is the acoustic velocity potential. We suppose that the velocity of wave propagation c is given by $c^{-2} = p - qe^{-\alpha y}$ in $y > 0$, where p, q, α are real and positive and $p > q$. It is equal to C' in the layer where C' is a constant. The method of dual integral transformation is used and the velocity potential ϕ is obtained after using asymptotic expressions for some of the functions which are in the integrand. We obtain the incident, reflected, multiply-reflected and diffracted pulses in the layer.

1. Introduction

Mishra[8] has considered the problem of propagation of two-dimensional sound pulses in an inhomogeneous semi-infinite medium. The line source has been supposed to be parallel to the Z-axis and located at $(0, y_0)$. The velocity of sound c is supposed to be given by $c^{-2} = (p - qe^{-\alpha y})$. The mixed initial boundary value problem has been solved by Friedlander's method of dual integral transformation.[3] Laplace transformation is applied with respect to time and Fourier transformation with respect to the space co-ordinate x. The solutions of the transformed equations are so chosen that they satisfy the doubly transformed boundary conditions and the boundedness condition at infinity. Then the Fourier inversion is performed and the solution is expressed in terms of certain integrals. These integrals are evaluated by the methods of steepest descents and contour integration to obtain the short-time approximations for the pulse in the illuminated and shadow regions respectively.

In this paper, we will consider the propagation of cylindrical sound pulses in the homogeneous layer $-y_0 \leqslant y \leqslant 0$. It is bounded on one side by an inhomogeneous plane stratified half space $y \geqslant 0$. The other boundary is either soft or rigid. It is supposed that the velocity of propagation c in $y > 0$ is a function of y only and is given by $c^{-2} = p - qe^{-\alpha y}$ where p, q, α are real and positive and $p > q$. The velocity in the layer is c' where c' is constant. The line source is parallel to the Z-axis and is located at $(0, -y_0)$ where $y_0 > 0$, in the layer. Due to the symmetry of the problem, it is sufficient to consider the case $x \geqslant 0$. Some of the rays that issue from the source $(0, -y_0)$, hit the interface $y = 0$. They are reflected back in the layer and refracted in the half space $y > 0$. The refracted rays proceed to infinity. The reflected rays hit the boundary $y = -y_1$ of the layer and are again reflected back in the layer. They hit the interface again and are refracted and reflected as in the first case. This process continues indefinitely. Similar will be the case when some of the rays that issue from the source, hit the boundary $y = -y_1$ and are reflected back in the layer. Now if $(p - q)^{-\frac{1}{2}} > c'$ there are some rays which hit $y = 0$ at such an angle that the refracted rays are tangential to it at the point of incidence.

Such refracted rays are called the glancing rays and the reflected rays at this point are called the critically reflected rays. The disturbance corresponding to these critical rays propagates along the reflector $y = 0$ with the higher velocity $(p - q)^{-\frac{1}{2}}$.[3, 5, 7] At every point of its path it sheds rays congruent to glancing rays in $y \geqslant 0$ and to critically reflected rays in the layer. These congruent rays in the layer hit $y = -y_1$, producing reflected rays in the layer. The reflected rays hit the interface again and produce glancing rays, etc. This process will be repeated *ad infinitum* (*see* Figs. 1 and 2).

We formulate the initial boundary value problem and use Friedlander's method of dual integral transformations. This leads to ordinary differential equations. We choose the solutions in such a way that they satisfy the doubly transformed boundary conditions and the boundedness condition at infinity. Performing Fourier inversion the solution is expressed in terms of certain integrals. If we follow Mishra[8] we shall get the approximate solutions in the regions $y > 0$ and the layer. But we are more interested in getting the solutions in the layer. The solution in this region is of greatest importance in Seismic exploration.[2] Hence in this paper we will find out the solution in the layer. Here we first perform the Laplace inversion to the integrals and get a double integral. Changing the order of integration we evaluate the integral after using the asymptotic expressions for the Bessel functions that occur in the integrals.[6]

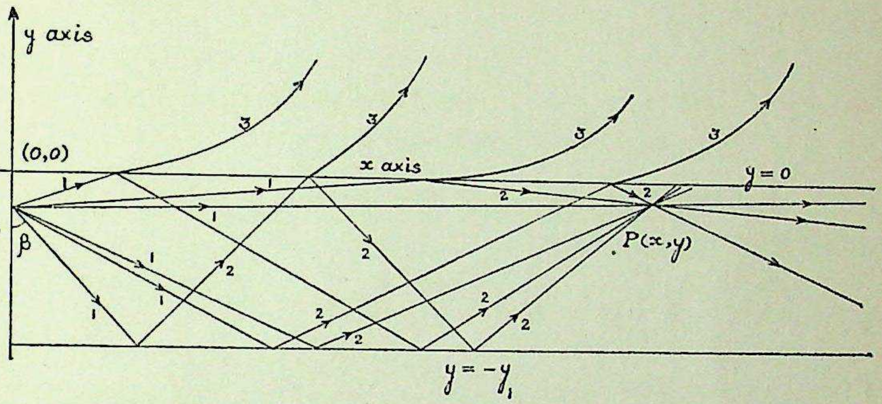

FIG. 1. The incident, reflected and refracted rays are marked by '1', '2', and '3', respectively in the layer $0 \geq y \geq -y_1$ and in the half space $y > 0$. Rays corresponding to τ_{rn} $\left(\begin{matrix} r = 0, n = 1, 2 \\ r = 1, n = 1, 2, 3, 4 \end{matrix}\right)$ are shown to reach a point P (x, y) in the layer.

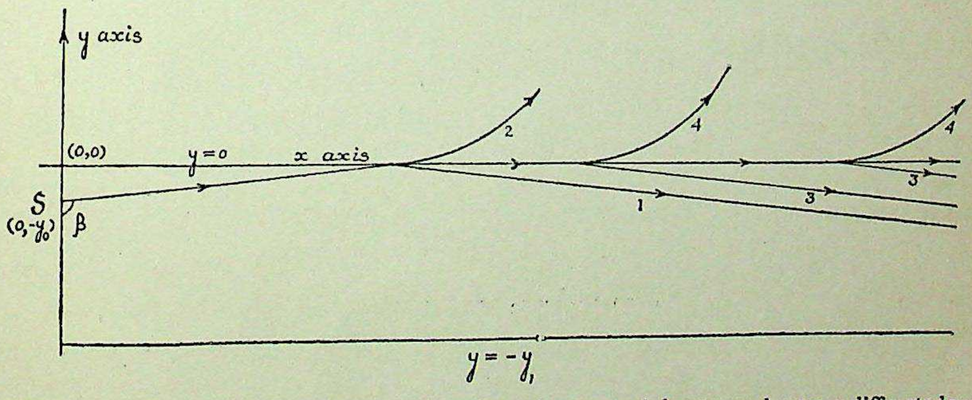

FIG. 2. The critically reflected and refracted rays and lower and upper diffracted rays, marked by '1', '2', '3', and '4' respectively, produced when the incident ray in $-y_0 \leq y \leq 0$ hits the interface at the critical angle.

2. FORMULATION OF THE PROBLEM

We consider the propagation of two-dimensional sound pulses in a homogeneous strip $-y_1 \leqslant y \leqslant 0$. It is bounded on one side by a semi-infinite inhomogeneous plane stratified medium $y \geqslant 0$. The other boundary is perfectly reflecting. Let a line source parallel to the Z-axis be located at $(0, -y_0)$, where $y_1 > y_0 > 0$. Then the acoustic velocity potential ϕ, the time integral of the pressure, will be independent of Z. We suppose that the density and the velocity of sound are ρ' and c' respectively when $-y_0 \leqslant y < 0$, ρ' and c' being constant. Let the velocity of sound c be given by

$$c^{-2} = p - qe^{-\alpha y}. \tag{2.1}$$

When $y > 0$, where p, q, α are real and positive and $p > q$. The density in $y > 0$ is supposed to be ρ where ρ is constant.

It is required to find ϕ as that function of x, y and time t which satisfies the wave equations

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} - (p - qe^{-\alpha y})\frac{\partial^2\phi}{\partial t^2} = 0, \ (y \geqslant 0) \tag{2.2}$$

and

$$\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2} - \frac{1}{c'^2}\frac{\partial^2\phi}{\partial t^2}$$

$$= -\,\delta(x)\,.\,\delta(y + y_0)\,.\,\delta(t), \ (-y_0 \leqslant y \leqslant 0), \tag{2.3}$$

the initial conditions

$$\phi = \frac{\partial\phi}{\partial t} = 0,$$

when

$$t = 0, \ x^2 + (y + y_0)^2 \neq 0, \tag{2.4}$$

and either of the boundary conditions at the surface $y = -y_1$

$$[\phi]_{y=-y_1} = 0 \tag{2.5}$$

or

$$\left[\frac{\partial\phi}{\partial y}\right]_{y=-y_1} = 0 \tag{2.6}$$

according as it is soft or rigid. In addition the conditions

$$\left[\frac{1}{\rho}\frac{\partial\phi}{\partial y}\right]_{y=+0} = \left[\frac{1}{\rho'}\frac{\partial\phi}{\partial y}\right]_{y=-0} \tag{2.7}$$

due to the continuity of the velocity at the interface and

$$\left[\frac{\partial\phi}{\partial t}\right]_{y=+0} = \left[\frac{\partial\phi}{\partial t}\right]_{y=-0} \tag{2.8}$$

due to the continuity of the pressure at the interface must be satisfied. The symbol δ in (2.3) stands for the Dirac δ-function.

3. The Formal Solution

To obtain the formal solution, we apply Laplace transformation and Fourier transformation to the wave equations and to the boundary conditions. We define the Laplace transformation $\bar{\phi}'$ of ϕ by

$$\bar{\phi}(x,y,s) = \int_0^\infty \phi(x,y,t)\, e^{-st}\, dt \tag{3.1}$$

and the Fourier transformation $\overset{*}{\phi}$ of $\bar{\phi}$ by

$$\overset{*}{\phi}(\mu, y's) = \frac{1}{(2\pi)^{\frac{1}{2}}} \int_0^\infty \bar{\phi}(x,y,s)\, e^{-i\mu x} dx. \tag{3.2}$$

It is easily seen that $\overset{*}{\phi}$ satisfies the equations

$$\frac{d^2\overset{*}{\phi}}{dy^2} - \{(\mu^2 + ps^2) - qs^2 e^{-\alpha y}\}\, \overset{*}{\phi} = 0, \quad (y \geqslant 0) \tag{3.3}$$

$$\frac{d^2\overset{*}{\phi}}{dy^2} - \left(\mu^2 + \frac{s^2}{c'^2}\right) \overset{*}{\phi} = \frac{\delta(y + y_0)}{(2\pi c)^{\frac{1}{2}}}, \quad (-y_1 \leqslant y \leqslant 0) \tag{3.4}$$

either of the boundary conditions

$$\overset{*}{\phi} = 0 \quad \text{or} \quad \frac{\partial\overset{*}{\phi}}{\partial y} = 0 \quad \text{at} \quad y = -y_1$$

and

$$[\overset{*}{\phi}]_{y=+0}^{y=-0} = 0, \quad \left[\frac{1}{\rho}\frac{d\overset{*}{\phi}}{dy}\right]_{y=+0} = \left[\frac{1}{\rho'}\frac{d\overset{*}{\phi}}{dy}\right]_{y=-0} \tag{3.5}$$

due to (2.7) and (2.8).

$\overset{*}{\phi}$ may be assumed to be continuous at $y = -y_0$. Then (3.4) is equivalent to

$$\frac{d^2\overset{*}{\phi}}{dy^2} - \left(\mu^2 + \frac{s^2}{c'^2}\right)\overset{*}{\phi} = 0 \tag{3.6}$$

$$[\overset{*}{\phi}]_{-y_0-0}^{-y_0+0} = 0, \quad \left[\frac{d\overset{*}{\phi}}{dy}\right]_{-y_0-0}^{-y_0+0} = -\frac{1}{(2\pi)^{\frac{1}{2}}}. \tag{3.7}$$

Therefore we wish to find, that solution of (3·3) and (3.6) which satisfy (3.5) and (3.7) and either of the boundary condition

$$\overset{*}{\phi} = 0 \quad \text{or} \quad \left(\frac{\partial\overset{*}{\phi}}{\partial y}\right) = 0 \quad \text{at} \quad y = -y_1.$$

If we impose the boundedness condition at infinity, we know that the solution of (3.3) is given by

$$\overset{*}{\phi}(\mu,y,s) = \mathrm{K}\mathrm{J}_v\left(\frac{2q^{\frac{1}{2}}s}{a}\ e^{-ay/2}\right), \quad (y \geqslant 0) \tag{3.8}$$

$$\nu = \frac{2}{a}(\mu^2 + ps^2)^{\frac{1}{2}} \tag{3.9}$$

where K is independent of y.

Also from (3.6) since c' is a constant

$$\overset{*}{\phi}(\mu,y,s) \begin{cases} = \mathrm{A}\exp.\left\{\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} y\right\} + \mathrm{B}\exp.\left\{-\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} y\right\}, \\ \qquad\qquad (-y_0 \leqslant y \leqslant 0) \qquad (3.10) \\ = \mathrm{C}\exp.\left\{\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} y\right\} + \mathrm{D}\exp.\left\{-\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} y\right\}, \\ \qquad\qquad (-y_1 \leqslant y \leqslant -y_0) \qquad (3.11) \end{cases}$$

where A, B, C and D are independent of y. Now we use (3.5), (3.7) and the boundary condition (2.6), we find after a short calculation that

$$\overset{*}{\phi}(\mu,y,s) = \frac{\cosh m(y_1 - y_0)\left\{\mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right)\rho m\cosh my - \rho' q^{\frac{1}{2}} s\,\mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)\sinh my\right\}}{m(2\pi)^{\frac{1}{2}}\left\{\mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right)\rho m\cosh my_1 + \rho' q^{\frac{1}{2}} s\,\mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)\cosh my_1\right\}}$$

$$(-y_0 \leqslant y \leqslant 0) \tag{3.12}$$

where

$$m = \left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}}. \tag{3.13}$$

If $-y_0 \geqslant y \geqslant -y_1$, then y and $-y_0$ must be interchanged in (3.12). We have not written the solution for $y \geqslant 0$ here because we are not going to find out the solution in this region in this paper. Now we perform Fourier inversion to (3.12) and get

$$\bar{\phi}(x.y,s) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\left\{\frac{\rho m \cosh my \mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right) - \rho' q^{\frac{1}{2}} s \sinh my \mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)}{\rho m \sinh my_1 \mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right) + \rho' q^{\frac{1}{2}} s \cosh my_1 \mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)}\right\}$$

$$\times \frac{\cosh m(y_1 - y_0)}{m} e^{i\mu x}\, d\mu. \tag{3.14}$$

We change $\cosh my$, $\sinh my$, $\sinh my_1$, and $\cosh my_1$, to exponential function and arrange the terms suitably in the integrand. Then we use binomial theorem to get

$$\bar{\phi}(x, y, s) = \sum_{r=0,\,1,\,2,\,\ldots,\,\infty} \bar{\psi}_r(x, y, s) \tag{3.15}$$

where

$$\bar{\psi}(x,y,s) \begin{cases} = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{\infty}\left\{\frac{\rho m \mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right) - \rho' q^{\frac{1}{2}} s\, \mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)}{\rho m \mathrm{J}_\nu\left(\frac{2q^{\frac{1}{2}}s}{a}\right) + \rho' q^{\frac{1}{2}} s\, \mathrm{J}_\nu'\left(\frac{2q^{\frac{1}{2}}s}{a}\right)}\right\}^r \\ \qquad \times \left\{\dfrac{e^{m(y-\overline{2r-1}\,y_1)} + e^{-m(y+\overline{2r+1}\,y_1)}}{m}\right\} \cosh m(y_1 - y_0)\, e^{i\mu x} d\mu, \\ \qquad\qquad (r = 1, 2, 3, 4 \ldots \infty) \\ = \dfrac{1}{2\pi}\displaystyle\int_{-\infty}^{\infty} \frac{\cosh m(y_1 - y_0)}{m} \exp.\{-m(y + y_1) + i\mu x\}\, d\mu; \quad (r = 0) \end{cases} \tag{3.16}$$

respectively. However we have assumed that term by term integration is allowed here for the expressions in (3.15). The solutions corresponding to the boundary condition (2.5) can be easily determined by applying the same method.

4. THE INCIDENT, REFLECTED AND DIFFRACTED PULSES

We assume s to be real positive and large. The Bessel function part of the integrand will be roughly independent of μ for $|\nu|$ very small. Therefore it seems quite reasonable to assume that the principal contributions to the integrals arise from large values of $|\nu|$. We know that the asymptotic expressions for Bessel functions are given by[1, 9]

$$\left.\begin{aligned} J_\nu(z') &\sim \frac{(\nu^2 - z'^2)^{-\frac{1}{4}}}{(2\pi)^{\frac{1}{2}}} \exp.\left\{(\nu^2 - z'^2)^{\frac{1}{2}} - \nu \cosh^{-1}\frac{\nu}{z'}\right\} \\ J_\nu'(z') &\sim \frac{(\nu^2 - z'^2)^{\frac{1}{4}}}{z'(2\pi)^{\frac{1}{2}}} \exp.\left\{(\nu^2 - z'^2)^{\frac{1}{2}} - \nu \cosh^{-1}\frac{\nu}{z'}\right\} \end{aligned}\right] \tag{4.1}$$

where v, z' are both large, $z' < v$. If we use the above approximations for Bessel functions in (3.15) we get

$$\bar{\phi}(x, y, s) \sim \frac{1}{4\pi}\int_{-\infty}^{\infty} \frac{e^{-m(y+y_0)} + e^{-m(2y_1-y_0+y)}}{\left(\mu^2 + \frac{s^3}{c'^2}\right)^{\frac{1}{2}}} e^{i\mu x} d\mu$$

$$+ \sum_{r=1,2,3,\ldots,\infty} \sum_{n=1,2,3,4} \bar{I}_{rn}(x, y, s) \tag{4.2}$$

where

$$\bar{I}_{rn}(x, y, s) = \frac{1}{4\pi}\int_{-\infty}^{\infty} f_{rn}(\mu) \exp.\{g_{rn}(\mu)\} d\mu \tag{4.3}$$

$$f_{rn}(\mu) = \frac{1}{\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}}} \left\{\frac{\rho\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} - \rho'(\mu^2 + \overline{p-q}\, s^2)^{\frac{1}{2}}}{\rho\left(\mu^2 + \frac{s^2}{c'^2}\right)^{\frac{1}{2}} + \rho'(\mu^2 + \overline{p-q}\, s^2)^{\frac{1}{2}}}\right\}^r \tag{4.4}$$

$$\left.\begin{aligned} g_{r_1}(\mu) &= -m(2ry_1 + y_0 + y) + i\mu x \\ g_{r_2}(\mu) &= -m(2ry_1 - y_0 - y) + i\mu x \\ g_{r_3}(\mu) &= -m(2ry_1 + 2y_1 - y_0 + y) + i\mu x \\ g_{r_4}(\mu) &= -m(2ry_1 - 2y_1 - y + y_0) + i\mu x \end{aligned}\right]. \tag{4.5}$$

Evidently the first two integrals in (4.2) are given by $\bar{I}_{r1}$ and $\bar{I}_{r2}$ if we put $r = 0$ there.

The approximations, that we have used, are for large values of s which means the short-time approximations for pulses and high-frequency approximations for harmonic waves. We see that the integrals, which we have in this case, are the same as we have when the inhomogeneous medium is taken as homogeneous with its sound velocity equal to the velocity of sound at the interface in the inhomogeneous medium.

Now let us evaluate one of the integrals in (4.2) say $\bar{I}_{r_1}(x,y,s)$. For this purpose we use the transformations $s = i\omega$ and $\mu = -is_1$. Thus we get

$$\bar{I}_{r_1}(x,y,s) = \frac{1}{4\pi}\int_{i\infty}^{-i\infty}\left\{\frac{\rho\left(s_1^2+\frac{\omega^2}{c'^2}\right)^{\frac{1}{2}} - \rho'\left(s_1^2+\overline{p-q}\,\omega^2\right)^{\frac{1}{2}}}{\rho\left(s_1^2+\frac{\omega^2}{c'^2}\right)^{\frac{1}{2}} + \rho'\left(s_1^2+\overline{p-q}\,\omega^2\right)^{\frac{1}{2}}}\right\}^r$$

$$\times\frac{1}{\left(s_1^2+\frac{\omega^2}{c'^2}\right)^{\frac{1}{2}}}\exp.\left\{s_1x - i\left(\frac{\omega^2}{c'^2}+s_1^2\right)^{\frac{1}{2}}\right.$$

$$\left.\times(2ry_1+y_0+y)\right\}ds_1. \qquad (4.6)$$

Let

$$x = l_{r_1}\cos\phi_{r_1};\ 2ry_1+y_0+y = l_{r_1}\sin\phi_{r_1}.$$

Then after the substitution

$$s_1 = -\frac{i\omega}{c'}\cos(\phi_{r_1}+iu)$$

in $\bar{I}_{r_1}$ we get when we perform the Laplace inversion

$$I_{r_1}(x,y,t) = \frac{1}{8\pi^2}\int_{-\infty}^{\infty}e^{i\omega t}\int_{-\infty}^{\infty}\left\{\frac{\rho\sin(\phi_{r_1}+iu) - \rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}{\rho\sin(\phi_{r_1}+iu) + \rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}\right\}^r$$

$$\times\exp.\left(-\frac{i\omega}{c'}l_{r_1}\cosh u\right)du\,.\,d\omega. \qquad (4.7)$$

If we change the order of integration and integrate first with respect to ω we get

$$I_{r_1}(x,y,t) = \frac{1}{4\pi}\int_{-\infty}^{\infty}\left\{\frac{\rho\sin(\phi_{r_1}+iu) - \rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}{\rho\sin(\phi_{r_1}+iu) + \rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}\right\}^r$$

$$\times\,\delta\left(t-\frac{l_{r_1}}{c'}\cosh u\right)du \qquad (4.8)$$

provided that $|\cos \phi_{r_1}| < c'(p-q)^{\frac{1}{2}}$. This condition is necessary because if this is not satisfied the original contour cannot be mapped into the hyperbolic path by the transformation from s_1 to u without crossing one of the branch lines from $\pm i\omega(p-q)^{\frac{1}{2}}$ to infinity. This condition is satisfied for all ϕ_{r_1} if $c' > (p-q)^{-\frac{1}{2}}$. Then integrating (4.8) we get the solution after breaking the integral into two parts and putting $l_{r_1}/c' \cosh u = \mathrm{V}$. In one part the limits of integration are from $-\infty$ to 0 and in the other from 0 to ∞ (*see* Figs. 3 and 4).

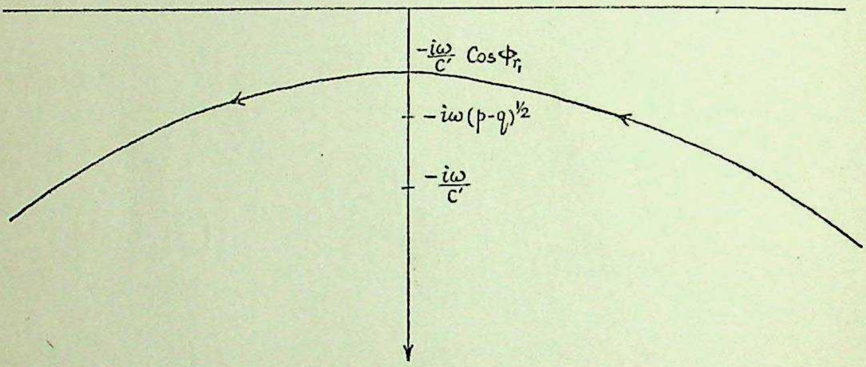
$-\frac{i\omega}{c'}\cos\phi_{r_1}$
$-i\omega(p-q)^{1/2}$
$-\frac{i\omega}{c'}$

FIG. 3

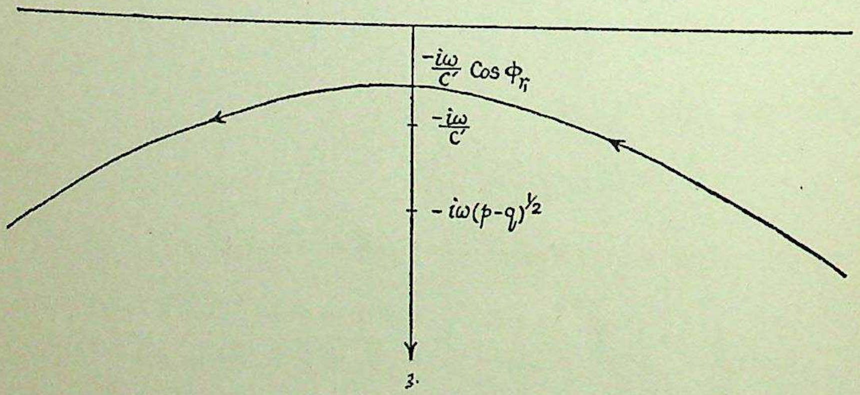
$-\frac{i\omega}{c'}\cos\phi_{r_1}$
$-\frac{i\omega}{c'}$
$-i\omega(p-q)^{1/2}$
3.

FIG. 4

Thus we get

$$\mathrm{I}_{r_1}(x, y, t) = \text{Real}\,\frac{1}{2\pi}\left\{\frac{\rho\sin(\phi_{r_1}+iu_{r_1}) - \rho'\left(\overline{p-q}\,c'^2 - \cos^2(\phi_{r_1}+iu_{r_1})\right)^{\frac{1}{2}}}{\rho\sin(\phi_{r_1}+iu_{r_1}) + \rho'\left(\overline{p-q}\,c'^2 - \cos^2(\phi_{r_1}+iu_{r_1})\right)^{\frac{1}{2}}}\right\}^{r}$$

$$\times\frac{\mathrm{H}\left(t-\frac{l_{r_1}}{c'}\right)}{\left(t^2-\frac{l_{r_1}{}^2}{c'^2}\right)^{\frac{1}{2}}}. \qquad (4.9)$$

We evaluate I_{r_2}, I_{r_3} and I_{r_4} as above and thus get

$$\phi(x, y, t) \sim \frac{H(t-\tau_{01})}{2\pi(t^2-\tau_{01}{}^2)^{\frac{1}{2}}} + \frac{H(t-\tau_{02})}{2\pi(t^2-\tau_{02}{}^2)^{\frac{1}{2}}} + \sum_{r=1,2,3,\ldots,\infty}\left[\sum_{n=1,2,3,4}\frac{H(t-\tau_{rn})}{2\pi(t^2-\tau_{rn}{}^2)^{\frac{1}{2}}}\right.$$

$$\left.\times \text{Real}\left\{\frac{\rho\sin(\phi_{rn}+iu_{rn})-\rho^1(\overline{p-q}\,c'^2-\cos^2(\phi_{rn}+iu_{rn}))^{\frac{1}{2}}}{\rho\sin(\phi_{rn}+iu_{rn})+\rho'(\overline{p-q}\,c'^2-\cos^2(\phi_{rn}+iu_{rn}))^{\frac{1}{2}}}\right\}^r\right] \quad (4.10)$$

where

$$\cosh u_{rn} = \frac{t}{\tau_{rn}}, \quad \tau_{rn} = \frac{l_{rn}}{c'}$$

l_{rn} is the expression corresponding to l_{r_1}.

Looking at (4.10) we see that the reflection coefficient is $+1$ at $y = -y_1$. This must be true here since the boundary $y = -y_1$ is rigid satisfying the Neumann conditions.

If

$$c' < \frac{1}{(q-q)^{\frac{1}{2}}} \quad \text{and} \quad \cos\phi_{rn} < c'(p-q)^{\frac{1}{2}},$$

no change is required; (4.10) continues to hold. When $\cos\phi_{rn} > c'(p-q)^{\frac{1}{2}}$ the path of integration can still be deformed into the hyperbolic path obtained from

$$S_1 = -\frac{i\omega}{c'}\cos(\phi_{rn}+iu)$$

provided that an additional portion round the branch point $-i(p-q)^{\frac{1}{2}}\omega$ which would have been crossed is joined on as illustrated in Fig. 5. The contribution of the hyperbolic path is same as in (4.8). The contribution of the remainder is obtained for $r \geqslant 1$ by making the substitution

$$S_1 = -\frac{i\omega\cos v}{c'}.$$

We have no such trouble when $r = 0$. Thus we get after evaluating this integral for $n = 1$

$$I_{r_1}(x, y, t) = \frac{H(l_{r_1}-c't)\,.\,H\left[\frac{c'}{(p-q)^{\frac{1}{2}}}t - c'x - \left(\frac{1}{p-q}-c'^2\right)^{\frac{1}{2}}(2ry_1+y_0+y)\right]}{2\pi\left(\frac{l_{r_1}{}^2}{c'^2}-t^2\right)^{\frac{1}{2}}}$$

$$\times \text{Imag.}\left\{\frac{\rho\sin v_{r_1}+i\rho'(\cos^2 v_{r_1}-c'^2\,\overline{p-q})^{\frac{1}{2}}}{\rho\sin v_{r_1}-i\rho'(\cos^2 v_{r_1}-c'^2\,\overline{p-q})^{\frac{1}{2}}}\right\}^r \quad (4.11)$$

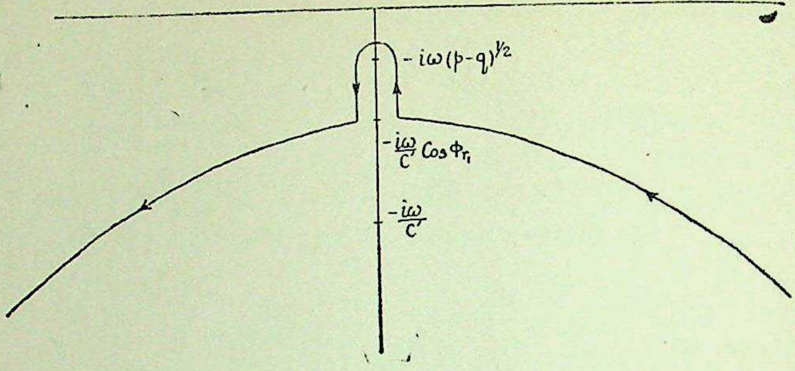

FIG. 5

where

$$l_{r_1}\cos(v_{r_1}-\phi_{r_1}) = c't.$$

If

$$c' = (p-q)^{-\frac{1}{2}},$$

the part

$$\left\{\frac{\rho\sin(\phi_{r_1}+iu)-\rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}{\rho\sin(\phi_{r_1}+iu)+\rho'\left(c'^2\,\overline{p-q}-\cos^2(\phi_{r_1}+iu)\right)^{\frac{1}{2}}}\right\}^r$$

of the integrand in (4.7) is a function of ρ and ρ' only and is equal to $\{(\rho-\rho')/(\rho+\rho'\})^r$. When $\rho'=\rho$ we see that this is zero. Therefore no reflection at $y=0$ is possible and the velocity potential is given by the first two terms of (4.10). When $\rho\neq\rho'$ reflection at $y=0$ will be there. We shall get the corresponding terms from (4.10) putting $c'=(p-q)^{-\frac{1}{2}}$ there. We further see that $c'(p-q)^{\frac{1}{2}}>\cos\phi_{r_1}$ for all $\phi_{r_1}\neq 0$, there is no need of additional contribution. (4.9) gives us the solution in this case. Since the critical case is not arising we are not getting diffracted pulses here.

Taking I_{r_2}, I_{r_3} and I_{r_4} into account we get the additional contribution (over and above 4.10)

$$\frac{1}{2\pi}\sum_{r=1,2,3,\ldots,a}\left[\sum_{n=1,2,3,4}\left[\frac{H(l_{rn}-c't)\,.\,H\left\{\frac{c'}{(p-q)^{\frac{1}{2}}}(t-\tau_{rn}{}^{*})\right\}}{(l_{rn}{}^2-t^2)^{\frac{1}{2}}}\right.\right.$$

$$\left.\left.\times\,\text{Imag.}\left\{\frac{\rho\sin v_{rn}+ip'(\cos^2 v_{rn}-c'^2\,\overline{p-q})^{\frac{1}{2}}}{\rho\sin v_{rn}-i\rho'(\cos^2 v_{rn}-c'^2\,\overline{p-q})^{\frac{1}{2}}}\right\}\right]\right]^r \qquad (4.12)$$

where

$$l_{rn}\cos(v_{rn}-\phi_{rn}) = c't, \quad (n = 1,\ 2,\ 3,\ 4)$$

$$\left.\begin{aligned}
\tau_{r_1}{}^* &= x(p-q)^{\frac{1}{2}} + \left(\frac{1}{c'^2}-p+q\right)^{\frac{1}{2}}(2ry_1+y_0+y)\\
\tau_{r_2}{}^* &= x(p-q)^{\frac{1}{2}} + \left(\frac{1}{c'^2}-p+q\right)^{\frac{1}{2}}(2ry_1+2y_1-y_0+y)\\
\tau_{r_3}{}^* &= x(p-q)^{\frac{1}{2}} + \left(\frac{1}{c'^2}-p+q\right)^{\frac{1}{2}}(2ry_1-y_0-y)\\
\tau_{r_4}{}^* &= x(p-q)^{\frac{1}{2}} + \left(\frac{1}{c'^2}-p+q\right)^{\frac{1}{2}}(2ry_1-2y_1-y+y_0)
\end{aligned}\right] \tag{4.13}$$

$$\left.\begin{aligned}
l_{r_1}{}^2 &= x^2+(2ry_1+y_0+y)^2\\
l_{r_2}{}^2 &= x^2+(2ry_1+2y_1-y_0+y)^2\\
l_{r_3}{}^2 &= x^2+(2ry_1-y_0-y)^2\\
l_{r_4}{}^2 &= x^2+(2ry_1-2y_1-y+y_0)^2
\end{aligned}\right]. \tag{4.14}$$

It is evident that I_{01} and I_{02} will not give us such additional contribution since the contours in them should not be deformed. There is no such branch point in these cases which are to be crossed.

Thus if $c't > l_{rn}$ the pulses are given by (4.10) only but if $t < l_{rn}/c'$ and $> \tau_{rn}{}^*$ the intensity of the pulses are given by (4.12) together with the incident pulses. The pulses given by (4.11) may be called diffracted pulses. Furthermore (4.10) and (4.12) are in complete agreement with the Geometrical Optics of the problem that follows in the next section. We can obtain the results similar to (4.10) and (4.12) if we take the surface $y = -y_1$ as soft, that is the Dirichlet's condition (2.5). The reflection coefficient at $y = -y_1$ will be (-1) in this case and this can be easily verified.

5. GEOMETRICAL OPTICS OF THE PROBLEM

Now we consider the Geometrical optics of the problem in order to interpret our results in terms of the geometrical theory of reflection and diffraction. The rays are given by the equation;

$$\frac{dy}{dx} = \pm\left\{\frac{1-\lambda^2c'^2}{\lambda^2c'^2}\right\}^{\frac{1}{2}} \tag{5.1}$$

and the arrival time $\tau(x, y)$ of the pulse is given by

$$\tau(x, y) = \int \lambda dx + \int \left(\frac{1}{c'^2} - \lambda^2\right)^{\frac{1}{2}} dy \tag{5.2}$$

where λ is a constant on a ray and is given by

$$\lambda = \frac{\sin \beta}{c'} . \tag{5.3}$$

Where β is the angle which the ray, that issues from the source $(0, -y_0)$, makes with the negative y-axis at the source (*see* Figs. 1 and 2). Let a ray hit the interface $y = 0$ at an angle of incidence θ, and let ϕ be the angle of refraction. Then $\sin \phi = K \sin \theta$ where

$$K = \frac{1}{c'(p-q)^{\frac{1}{2}}} .$$

If $K \leqslant 1$, ϕ is real for all θ and hence all the rays that hit the interface will be refracted in the upper medium. If $K > 1$, ϕ is real only when $K \sin \theta \leqslant 1$.

When $\pi \geqslant \beta > \pi/2$ the rays that issue from the source, strike the interface $y = 0$. They are reflected and refracted according to the laws of geometrical optics if $K \leqslant 1$. If $K > 1$ these rays are reflected and refracted as above if $K \sin \theta \leqslant 1$. The refracted rays enter in $y > 0$ and proceed to infinity. The reflected rays hit the boundary $y = -y_1$ and are again reflected. They strike the interface $y = 0$ again and are reflected and refracted as in the first case. This process continues *ad infinitum*. When $0 \leqslant \beta < \pi/2$ the rays hit the boundary $y = -y_1$, and are reflected as in the case when $\pi/2 < \beta \leqslant \pi$. If $\beta = \pi/2$, the ray proceeds to $x = \infty$ parallel to X-axis.

We note that when $K > 1$ and $K \sin \theta = 1$ we have $\phi = \pi/2$ so the refracted ray is tangential to $y = 0$ at this point. This ray is called the critically refracted ray or the glancing ray. The reflected ray at the point may be called the critically reflected ray. When $K > 1$, $K \sin \theta > 1$, there is no real value of ϕ and hence there is no refracted rays. Thus we have total reflection in this case and the region in the upper medium bounded by the glancing ray and the segment (x', ∞) of the X-axis, x' being the point of tangency of the glancing ray, may be called the 'shadow'. However by the geometrical theory of diffraction the disturbance propagates along the interface $y = 0$ with constant velocity $(p - q)^{-\frac{1}{2}}$. This is called the surface wave. At each point of its path the surface pulse splits into three parts. One continues along the surface as before while the second leaves it tangentially along a ray determined by (5.1). We shall call it the upper diffracted ray. They are congruent to the critically reflected ray. These rays may be called the lower diffracted rays. These diffracted rays hit $y = -y_1$, and are reflected. The reflected rays hit $y = 0$ and thus produce critically reflected and refracted rays. Thus we have again surface pulses giving rise to diffracted pulses. This process will continue indefinitely. Thus in the layer $-y_1 \leqslant y \leqslant 0$, we may have incident 'reflected' multiply-reflected pulses together with diffracted and multiply-diffracted pulses reaching a point.

Now in the layer the ray that issues from the source at an angle β is given by (5.1) as

$$x + (y + y_0) \tan \beta = 0, \quad \left(0 \leqslant \beta < \frac{\pi}{2}\right). \tag{5.4}$$

This ray, after r reflections from $y = 0$ and $(r + 1)$ reflections from $y = -y_1$ has its equation given by

$$x + \{y + (2r + 2)\, y_1 - y_0\} \tan \beta = 0, \quad (r \geqslant 0) \tag{5.5}$$

and its equation after r reflections from $y = 0$ and $y = -y_1$ is given by

$$x + (y - 2ry_1 + y_0) \tan \beta = 0 \qquad (r \geqslant 1). \tag{5.6}$$

When $\pi/2 < \beta < \pi$ the incident ray is given by

$$x + (y + y_0) \tan \beta = 0. \tag{5.7}$$

We get the equation of the ray after r reflections from $y = 0$ and $y = -y_1$ as

$$x + (y + 2ry_1 + y_0) \tan \beta = = 0 \qquad (r \geqslant 0). \tag{5.8}$$

The same equation of the ray after $(r - 1)$ reflections from $y = y_1$ and after r, reflections from $y = 0$ is given by

$$x - \{y - 2\,(r - 1)\, y_1 - y_0\} \tan \beta = 0, \quad (r \geqslant 1). \tag{5.9}$$

When $\beta = \pi/2$ the ray is given by $y = -y_0$. This neither hits $y = 0$ nor $y = -y_1$. It is parallel to x-axis.

Now when $\sin \beta = c'\,(p - q)^{\frac{1}{2}}$ the reflected ray at $y = 0$ becomes the critically reflected ray. Hence when $0 \leqslant \beta < \pi/2$ the critically reflected ray is given by

$$x + (y + y_0 - 2ry_1)\,(p - q)^{\frac{1}{2}} \left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}} = 0, \quad (r \geqslant 1). \tag{5.10}$$

Similarly when $\pi/2 < \beta \leqslant \pi$ these rays are given by

$$x + \{y - 2(r-1)y_1 - y_0\}(p-q)^{\frac{1}{2}}\left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}}, \quad (r \geqslant 1). \tag{5.11}$$

Therefore the lower diffracted rays corresponding to (5.10) and (5.11) are given by

$$x = \delta' - (y - 2ry_1 + y_0)(p-q)^{\frac{1}{2}}\left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}} \tag{5.12}$$

and

$$x = \delta'' - \{y - 2(r-1)y_1 - y_0\}(p-q)^{\frac{1}{2}}\left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}} \tag{5.13}$$

respectively, where

$$\delta' = (x_0' - x') \quad \text{and} \quad \delta'' = (x_0'' - x''),$$

$(x_0, 0)$ is the point from which emanate the rays congruent to the critically reflected rays which strike the interface at $(x_1'\ 0)$ and $(x_1''\ 0)$ respectively. The lower diffracted rays strike $y = -y_1$ and are reflected. The equation of these reflected rays are given by

$$x = \delta' + \{2(r+1)y_1 + y - y_0\}(p-q)^{\frac{1}{2}}\left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}} \tag{5.14}$$

and

$$x = \delta'' + \{2ry_1 + y + y_0\}(p-q)^{\frac{1}{2}}\left(\frac{1}{c'^2} - p + q\right)^{-\frac{1}{2}}. \tag{5.15}$$

We can also find out the equations of the rays after any number of erflections from $y = -y_1$ or $y = 0$. But we are not concerned with them in the present paper.

The arrival times of these pulses are found out by using (5.2) or independently. Corresponding to the rays given by (5.8), (5.5), (5.6), (5.9), (5.15), (5.14), (5.12) and (5.13) we get their arrival times as

$$\tau_{r_1} = \lambda x + \left(\frac{1}{c'^2} - \lambda^2\right)^{\frac{1}{2}}(2ry_1 + y_0 + y) = \frac{l_{r_1}}{c'} \tag{5.16}$$

$$\tau_{r_2} = \lambda x + \left(\frac{1}{c'^2} - \lambda^2\right)^{\frac{1}{2}}(2ry_1 + 2y_1 - y_0 + y) = \frac{l_{r2}}{c'} \tag{5.17}$$

$$\tau_{r_2} = \lambda x + \left(\frac{1}{c'^2} - \lambda^2\right)^{\frac{1}{2}} (2ry_1 - y_0 - y) = \frac{l_{r_3}}{c'} \tag{5.18}$$

$$\tau_{r_4} = \lambda x + \left(\frac{1}{c'^2} - \lambda^2\right)^{\frac{1}{2}} (2ry_1 - 2y_1 - y + y_0) = \frac{l_{r_4}}{c'} \tag{5.19}$$

$$\tau_{r_1}{}^* = (p - q)^{\frac{1}{2}}\, x + \left(\frac{1}{c'^2} - p + q\right)^{\frac{1}{2}} (2ry_1 + y_0 + y) \tag{5.20}$$

$$\tau_{r_2}{}^* = (p - q)^{\frac{1}{2}}\, x + \left(\frac{1}{c'^2} - p + q\right)^{\frac{1}{2}} (2ry_1 + 2y_1 - y_0 + y_1) \tag{5.21}$$

$$\tau_{r_3} = (p - q)^{\frac{1}{2}}\, x + \left(\frac{1}{c'^2} - p + q\right)^{\frac{1}{2}} (2ry_1 - y - y_0) \tag{5.22}$$

$$\tau_{r_4}{}^* = (p - q)^{\frac{1}{2}}\, x + \left(\frac{1}{c'^2} - p + q\right)^{\frac{1}{2}} (2ry_1 - 2y_1 - y + y_0). \tag{5.23}$$

respectively, where we take $r \geqslant 0$ for (5.16) and (5.17) and $r \geqslant 1$ for the rest.

We see that τ_{rn} stand for the arrival times of the incident and reflected pulses along the rays that hit the interface $y = 0$, r times. We have $n = 1$, 2, 3 and 4 which correspond to the arrival times along the rays that hit $y = -y_1$, r, $(r + 1)$, r and $(r - 1)$ times respectively when $r \geqslant 1$. We also have $n = 1$ and 2 which correspond to arrival times along the rays that do not hit $y = -y_1$, and hit $y = -y_1$ once, respectively when $r = 0$. $\tau_{rn}{}^*$ correspond to the arrival times of the lower diffracted pulses.

Now we can interpret the solutions obtained in the last section. From (5.16) to (5.19) we find that τ_{rn} defined by (4.9) are the arrival times of the incident, reflected and multiply-reflected pulses. From (5.20) to (5.23) we find that $\tau_{rn}{}^*$ defined by (4.13) are the arrival times of the diffracted pulses at a point (x, y, t) in the layer where t satisfies the conditions given by

$$\tau_{rn}{}^* < t < \frac{l_{rn}}{c'}.$$

This has already been explained in Section 4.

6. CONCLUSION

We have obtained the solutions of the problem and interpreted them as incident, reflected, multiply-reflected and diffracted pulses in terms of geometrical theory of acoustics. It also includes the geometrical theory of diffraction as given by Keller,[7] Grimshaw,[5] and others.[2] The diffracted waves are also called the lateral waves.[2] We have used approximations for large values of s which means short-time approximations for the pulses and high-frequency approximations for the harmonic case. We see that for large values of s the behaviour of the pulse in the layer is not changed whether the upper half space is homogeneous or inhomogeneous when the inhomogeneous half space should have its velocity at the interface equal to the velocity of the homogeneous half space.

We may get the solutions by applying the method of steepest-descents and its modified form. But we obtain the exact solutions of the problem for large s. Therefore it is more accurate though the method is not so widely applicable.

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GROWTH OF WEAK DISCONTINUITIES IN ARBITRARILY MOVING GAS

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ABSTRACT

The theory of singular surfaces is combined with the ray theory to the study of anisotropic, non-linear wave-propagation in an arbitrarily moving gas. The governing equation for the strength of the wave along the rays is expressed in an integral form. Use of the analysis is made by working out two examples in detail.

1. INTRODUCTION

USING the theory of singular surfaces Thomas[1] investigated the propagation of weak discontinuities in ideal gases. He derived the growth equation and discussed the conditions under which the discontinuities either terminate into a shock or decay out. By the same method Kaul[2] studied the propagation of weak discontinuities in ideal gases by considering the entropy and the sound speed as dependent variables instead of pressure and density. The propagation is found, by both of them, to be isotropic in character. The reason for this is that the medium ahead of the wave surface is assumed to be uniform and at rest. If the medium ahead is moving, then it can be shown[3] that the wave propagation is anisotropic.

To study the anisotropic wave propagation Lighthill[4] developed an elegent method which essentially involves the evaluation of the Fourier integrals by stationary phase method and it gives the asymptotic features of the solution. Many applications of this method followed. Ludwig[5] and Duff[6] further generalised and developed this technique.

In this investigation firstly we found that the theory of singular surfaces and the method of geometrical optics (ray theory) due to Luneberg[7] can be combined to study the propagation of weak discontinuities in non-linear anisotropic media. This combination enables one to obtain and integrate the equation of growth of the discontinuity in a simple and straightforward manner. Secondly we apply this method to study the propagation of weak discontinuities in self-gravitating moving ideal gas. The ray equations and the other formulae that are found to be quite useful to integrate the growth equation are given in Section 2. In Section 3, the basic equations for self-gravitating ideal gas are studied. When the medium ahead of the discontinuity is assumed to be time-independent and also arbitrarily moving then the wave propagation is found to be anisotropic. In Section 4 the growth equation for such discontinuity is derived and an integral representation of the strength of the discontinuity is also obtained. If the medium ahead of the wave is known, then this integral can be evaluated.

To illustrate the method, the critical time or distance for the shock formation is calculated in the two cases (i) when the medium ahead is that of a polytropic self-gravitating gas spheres, and (ii) where the two and the three-dimensional radial flow of an inviscid compressible fluid is supposed to be taking place.

2. WAVE-FRONTS AND RAYS

We consider a moving surface $\Sigma(t)$ which is described by the equation of either of the forms

$$f(x_i, t) = 0, \quad x_i = x_i(y^{\alpha}, t). \tag{1}$$

Here x_i are the cartesian co-ordinates of a point on the surface $\Sigma(t)$, t is the time and y^{α} is any system of Gaussian surface co-ordinates. We employ the cartesian tensor notation throughout. A Latin index takes the values 1, 2, 3 and the Greek one 1, 2. A comma preceding a Latin index will denote partial differentiation with respect to x_i and when it precedes a Greek one, it denotes covariant differentiation with respect to y^{α}. We name the surface a singular surface when all the field variables are continuous across it. We always denote $g_{\alpha\beta}$, $b_{\alpha\beta}$, the first and second fundamental forms of the surface respectively. Let n_i be the components of a unit normal to the surface $\Sigma(t)$ considered positive when it points into the medium ahead of it and G the velocity with which it moves along the normal trajectory. We then denote the jump of any quantity z across $\Sigma(t)$ by

$$[z] = z_1 - z_0, \tag{2}$$

where z_0 is the value of z ahead of $\Sigma(t)$ and z_1 is its value just behind.

In order to relate the singular surface theory with the ray theory, we first observe that the derivative with respect to time t of any function $F(x_i, t)$ along the normal trajectory is given by

$$\frac{\delta F}{\delta t} = \frac{\partial F}{\partial t} + F_{,i}\, G n_i. \tag{3}$$

Since n_i is orthogonal to the wave surface, this $\delta/\delta t$ commutes with tangential differentiation. Further, if V_i denotes the velocity in any direction (which we identify later with ray direction), then the derivative of F along this direction is given by

$$\frac{d_r F}{dt} = \frac{\delta F}{\delta t} + F_{,i}\, V_i \tag{4}$$

From (3) and (4) we obtain the first basic relation we use in our problem as

$$\frac{d_r F}{dt} = \frac{\delta F}{\delta t} + F_{,i}(V_i - G n_i). \tag{5}$$

Here we note that this relation holds good for jumps too. If $\partial f/\partial t \neq 0$, then we can assume the equation to the wave surface in the form

$$f = W(x_i) - t. \tag{6}$$

Now if we identify F with f; then since the latter continues to represent the wave-front, it follows that $\delta f/\delta t = 0$. So from (3) and (6) we get

$$\mathscr{H} = GN - 1 = 0, \tag{7}$$

where $N_i = f_{,i}$ so that $N_i = N n_i$.

Now (7) is a first-order partial differential equation for the equation of the wave-front $\Sigma(t)$. Its solution is obtained by solving a system of ordinary first-order differential equation for x_i and N_i, regarded as independent, given by

$$\frac{dx_i}{dt} = \frac{\partial \mathcal{H}}{\partial N_i}, \tag{8}$$

$$\frac{dN_i}{dt} = \frac{\partial \mathcal{H}}{\partial x_i}. \tag{9}$$

Here t can be any parameter describing the curves defined as rays given by (8) and (9). So the time derivatives that appear here are differentiation with respective to t along rays. Thus these derivatives are the same as d_r/dt in our notation. Now if we identify the direction mentioned in (4) with ray direction, then from (7), (8) and (9) we obtain the ray equation as:

$$V_i = \frac{d_r x_i}{dt} = G n_i + (\delta_{ij} - n_i n_j) \frac{\partial G}{\partial n_j}, \tag{10}$$

$$\frac{d_r n_i}{dt} = (n_i n_j - \delta_{ij}) \frac{\partial G}{\partial n_j}. \tag{11}$$

From (7) and (10) it readily follows that

$$G = V_i n_i, \qquad V_i N_i = 1. \tag{12}$$

The ray velocity V_i has always tangential components in the case of anisotropic wave propagation and this is given by the second term of (10). In general G is a function of both x_i and n_i which are in term functions of t as we move along the rays. So the variation of G along rays is given by

$$\frac{d_r G}{dt} = \frac{\partial G}{\partial x_i} \frac{d_r x_i}{dt} + \frac{\partial G}{\partial n_i} \frac{d_r n_i}{dt}. \tag{13}$$

Using (10), (11) and (12) we obtain from (13) a useful relation

$$\begin{aligned} \frac{d_r \log G}{dt} &= \frac{\partial G}{\partial x_i} n_i \\ &= V_{i,j}\, n_i\, n_j. \end{aligned} \tag{14}$$

Another useful relation we make use is

$$\frac{d_r}{dt} \log (EG) = V_{i,i}, \tag{15}$$

where E is the expansion ratio (*see* Appendix).

3. BASIC EQUATIONS

We consider an ideal gas under its own gravitation. We denote the velocity, pressure and density of the gas by u_i, p and ρ respectively. Then the equations governing the flow of such gas are

$$\frac{\partial \rho}{\partial t} + u_i \rho_{,i} + \rho u_{i,i} = 0, \tag{16}$$

$$\rho\left(\frac{\partial u_i}{\partial t} + u_j u_{i,j}\right) + p_{,i} - \rho \Phi_{,i} = 0, \tag{17}$$

where Φ is the gravitational potential satisfying the equation

$$\Phi_{,ii} = -4\pi\rho g. \tag{18}$$

In (18) g denotes the acceleration due to gravity. We can show easily that the entropy is continuous across a moving wave-front. So we have not taken the energy equation into consideration and also the pressure is now taken to be a function of the density only.

Now we wish to study the propagation of weak discontinuities by which we mean that the field variables describing the medium are themselves continuous across it while their derivatives may be discontinuous. Thus we have

$$[u_i] = 0, \quad [p] = 0, \quad [\rho] = 0, \quad [\Phi_{,i}] = 0, \quad [\Phi_{,ij}] = 0. \tag{19}$$

We now derive the expressions for the propagation speed G and the ray velocity V_i. For this we first take the jumps of (16) and (17). Then making use of the first-order compatibility conditions (8) and (19) we obtain

$$(G - u_{on})\,\eta - \rho_o \lambda_n = 0, \tag{20}$$

$$\rho_o (G - u_{on})\,\lambda_i - a^2 \eta n_i = 0, \tag{21}$$

where

$$[u_{i,j}]\, n_j = \lambda_i, \ [\rho_{,i}]\, n_i = \eta. \tag{22}$$

The isentropic sound speed in the medium ahead $\Sigma(t)$ is denoted by $a^2 = \gamma p_o/\rho_o$ where γ is the ratio of specific heats. The time-independent variables u_{oi}, p_o, ρ_o and Φ_o which describe the medium ahead, satisfy the equation

$$u_{oj}u_{oi,j} - \Phi_{o,i} = \frac{a^2\rho_{o,i}}{\rho_o}, \quad \Phi_{o,ii} = -4\pi\rho_o g. \tag{23}$$

Elimination of η in between (20) and (21) yields

$$(G - u_{on})^2 \lambda_i = a^2\lambda_j n_j n_i. \tag{24}$$

Since $\lambda_i \neq 0$ by our assumption of weak discontinuity, we get from (24) the propagation speed as

$$G = u_{on} + a. \tag{25}$$

This expression shows that due to the motion of the gas ahead of $\Sigma(t)$ G depends on both x_i and n_i which clearly indicates the anisotropic character of the propagation.

Now from (10) and (25) we obtain the ray velocity as

$$V_i = u_{oi} + an_i. \tag{26}$$

When the medium ahead is at rest then the propagation speed reduces to that of sound speed and then rays coincide with normal trajectories. From (20), (21) and (25) we get

$$\lambda_i = \lambda n_i, \quad \lambda = \lambda_i n_i, \quad \eta = \frac{\rho_o\lambda}{a}. \tag{27}$$

We define the scalar λ which gives the jump of the divergence of the velocity as the strength of the discontinuity.

Since $\lambda_i = \lambda n_i$ it follows that the vorticity is continuous across the wavefront. Thus the wave is an irrotational one.

Moreover we have

$$g^{\alpha\beta}\lambda_{i,\alpha}x_{i,\beta} = -2\lambda\Omega, \tag{28}$$

where Ω is the mean curvature of the surface defined by

$$2\Omega = g^{\alpha\beta}b_{\alpha\beta}. \tag{29}$$

In deriving (28) we made use the Weingarten formula

$$n_{i,\alpha} = -b_\alpha^{\beta}x_{i,\beta}, \tag{30}$$

Also we can easily show that

$$n_i \frac{\delta \lambda_i}{\delta t} = \frac{\delta \lambda}{\delta t}, \quad n_i \frac{d_r \lambda_i}{dt} = \frac{d_r \lambda}{dt}, \tag{31}$$

and

$$\frac{d_r \mathrm{F}}{dt} = \frac{\delta \mathrm{F}}{\delta t} + u_o{}^a \, \mathrm{F}_{,a}. \tag{32}$$

Relation (32) is obtained from (5) and (26).

4. GROWTH EQUATION

Now we differentiate (16) with respect to x_j and multiply with n_j. Then taking the jumps and making use of the second-order compatibility conditions,[8] we get

$$a\bar{\eta} - \rho_o \bar{\lambda}_n = \frac{d_r \eta}{dt} + \mathrm{A}, \tag{33}$$

where

$$[u_{i,\, jk}]\, n_j n_k = \bar{\lambda}_i, \quad [\rho,\, _{jk}]\, n_j n_k = \bar{\eta}, \tag{34}$$

$$\mathrm{A} = \left(2\rho_{o,\,i}\, n_i n_i + \frac{\rho_o}{a}\,(u_{oi,\,i} + u_{oi,\,j}\, n_i n_j) - 2\rho_o \Omega\right)\lambda + \frac{2\rho_o}{a}\,\lambda^2 \tag{35}$$

Similarly we differentiate (17) with respect to x_j and multiply by $n_i n_j$ and then by taking jump we obtain

$$a\,(\rho_o \bar{\lambda}_n - a\bar{\eta}) = \rho_o \frac{d_r \lambda}{dt} + \mathrm{B}, \tag{36}$$

where

$$\mathrm{B} = \rho_o \left\{(2u_{oi,\,j}\, n_i n_j + \left(2\Upsilon - 3 + \frac{1}{\rho_o}\right) a\rho_{o,\,i}\, n_i\right\} \lambda + (\Upsilon - 1)\, \rho_o \lambda^2 \tag{37}$$

In obtaining (33) and (35) use of (23), (25), (28) and (32) has been made. Now eliminating $\bar{\lambda}_n$ and $\bar{\eta}$ in between (33) and (35) and then using the relation $\eta = \rho_o/\lambda a$, we obtain the equation for λ which we call the *growth equation* as

$$\frac{d_r\lambda}{dt} + C\lambda + \frac{\gamma+1}{2}\lambda^2 = 0, \tag{38}$$

where

$$2C = \frac{d_r}{dt}\log\left(\frac{\rho_o}{a}\right) + 3u_{oi,j}\,n_in_j + u_{oi,i} + 4a_{,i}n_i - 2a\Omega. \tag{39}$$

When the medium ahead is uniform and at rest, then the equation (38) reduces to the growth equation obtained by Thomas.[1]

Now from (14), (15), (25) and (26) we get

$$\frac{d_r}{dt}\log G = u_{oi,j}\,n_in_j + a_{,j}\,n_j, \tag{40}$$

$$\frac{d_r}{dt}\log(EG) = u_{oi,i} + a_{,i}\,n_i - 2a\,\Omega. \tag{41}$$

With the help of (41) and (40) we can write (39) as

$$2C = \frac{d_r}{dt}\log\left(\frac{\rho_o EG^4}{a}\right) \tag{42}$$

Substituting the value for C from (42) in (38) and then integrating we get

$$\frac{1}{\lambda D} - \frac{1}{\lambda_o D_o} = \frac{\gamma+1}{2}\int_0^t \frac{dt}{D}, \tag{43}$$

where

$$D = \left(\frac{\rho_o EG^4}{a}\right)^{\frac{1}{2}}, \tag{44}$$

and λ_o, D_o denote the values of λ and D at $t = 0$ respectively. If the medium ahead is known, the integral in (43) can then be evaluated.

We believe that the method we have given in this paper is quite general and can be successfully applied to investigate the anisotropic wave propagation in any continuum media. In fact some of us[9-13] have already investigated the anisotropic wave propagation in elastic medium (conducting and non-conducting).

5. EXAMPLES

In this section we illustrate how the critical time for the shock formation can be calculated with the help of (43) when the medium ahead is not uniform. The first example is taken from the astrophysics. The medium ahead is that of a polytropic self-gravitating gas spheres. The steady state spherically-symmetric equations are (Eddington[14])

$$\frac{1}{\rho}\frac{dp}{dr} + \frac{Gm}{R^2} = 0, \quad \frac{dm}{dR} = 4\pi R^2 \rho, \quad \frac{p}{p_0} = \left(\frac{\rho}{\rho_0}\right)^{\gamma}, \tag{45}$$

where quantities with suffix zero denote the corresponding values at $R = 0$, R being the radius of the star. Introducing the dimensionless variables defined by

$$P = \frac{p}{p_0}, \quad \chi = \frac{\rho}{\rho_0}, \quad z = \frac{R}{R_0}, \quad R_0 = \frac{3a_0^2}{2\pi\rho_0 G}, \quad a_0^2 = \frac{\gamma p_0}{\rho_0},$$

$$M = \frac{m}{\frac{4}{3}\pi\rho_0 R_0^3}, \tag{46}$$

into (45), we get (Sakurai[16])

$$\frac{d}{dz}\left(z^2 \chi^{\gamma-2} \frac{d\chi}{dz}\right) + 6z^2\chi = 0. \tag{47}$$

Solution of (47) for various values of γ has been obtained (Eddington, pp. 82–83). For small z, we get (Sakurai,[16] equations 26–30)

$$\chi = 1 - z^2 + \frac{(13 - 15\gamma)}{10} z^4 + \cdots, \tag{48}$$

$$\rho = 1 - \gamma z^2 + \tfrac{4}{5} \gamma z^4 + \cdots, \tag{49}$$

$$M = z^3 \left(1 - \frac{3}{5} z^2 + \frac{39 - 15\gamma}{70} z^4 + \cdots\right), \tag{50}$$

$$\frac{a^2}{a_0^2} = 1 - (\gamma - 1) z^2 + 0{\cdot}3 (\gamma - 1) z^4 + \cdots. \tag{51}$$

From (43), the critical time for the shock formation is given by

$$\frac{1}{\lambda_0} = -\frac{\gamma + 1}{2} \int_0^t \frac{D_0}{D}\, dt, \tag{52}$$

In this case $u_n = 0$, $G = a$, $E/E_0 = z^2$. Let $a_0 t = R = R_0 z$, and t equal to zero may be taken at $z = 0{\cdot}25$. (52) now becomes

$$-\frac{a_0}{\lambda_0 R_0} = \frac{\gamma + 1}{2} \int_{0\cdot25}^{z} \frac{\chi}{p^{3/2}} \frac{dz}{z}. \tag{53}$$

With the help of (48) to (51), we get from (53) valid for small z (*cf.* Thomas[1]).

$$-\frac{a_0}{\lambda_0 R_0} = \frac{\gamma + 1}{2} \left\{\log \frac{z}{0\cdot25} + \left(\frac{3}{2}\gamma - 1\right)\frac{1}{2}(z - 0\cdot25)^2\right\} \tag{54}$$

Equation (53) is numerically integrated for $\gamma = 1{\cdot}4$ and in Table I are given the values of $a_0/\lambda_0 R_0$ for $z = 0{\cdot}25$ to 2. For higher values of $z\,(> 0{\cdot}75)$, χ, ρ are taken from Eddington's book.[14]

TABLE I

z	0·25	0·5	0·75	1	1·25	1·5	1·75	2
$-a_0/\lambda_0 R_0$	zero	0·06	1·60	2·1	2·57	3·07	3·62	4·30

In the second example the medium ahead the shock waves is prescribed as the one where the two- and the three-dimensional radial flow of an inviscid, compressible fluid is supposed to be taking place (Levey[15] and Sakurai[17]). The equations describing the flow are

$$\rho u r^n = \text{const.}, \quad \rho u \frac{du}{dr} + \frac{dp}{dr} = 0, \quad \frac{p}{p_1} = \left(\frac{\rho}{\rho_1}\right)^{\gamma}. \tag{55}$$

($n = 1$, for cylindrical case and $n = 2$ for spherical). The quantities with subscript 1 are their corresponding values at $r = r_1$, r_1 is the characteristic length. We define $\omega = u/a_1$, $r' = r/r_1$, $\rho' = \rho/\rho_1$, $a_1 = \gamma p_1/\rho_1$, $\rho_1 a_1 r_1{}^n = \rho u r^n$. Multiplying the second equation (55) by ur^n and introducing the dimensionless variables, we obtain

$$\frac{d}{dr'}\left(\frac{\omega^2}{2}\right) + \frac{1}{\gamma - 1}\frac{d}{dr'}(\rho'^{\gamma-1}) = 0. \tag{56}$$

Equation (56) on integration becomes ($\omega = 1$, $r' = 1$)

$$\frac{\omega^2}{2} + \frac{1}{\gamma - 1}\left(\frac{1}{\omega r'^n}\right)^{\gamma-1} = \frac{\gamma + 1}{2(\gamma - 1)}. \tag{57}$$

Equation (56) can also be written as

$$\frac{d\omega}{dr'} = \frac{n\omega}{r'}\left\{\frac{1-\beta\omega^2}{\omega^2-1}\right\}, \quad \beta = \frac{\gamma-1}{\gamma+1}. \tag{58}$$

Here $G = u_n + a$ (25), $E/E_0 = r'^n$, hence $G/G_0 = \omega + 1$,

$$\frac{a^2}{{a_1}^2} = \rho^{\gamma-1} \text{ and } a_1 t = r = r_1 r'.$$

The equation (52) reduces in terms of ω as

$$-\frac{a_1}{r_1\lambda_0} = \frac{\gamma+1^2}{2}\int_1^{\omega} \frac{\omega-1}{\omega+1}\cdot\frac{d\omega}{n\omega}\cdot\left(\frac{\gamma+1}{2} - \frac{\gamma-1}{2}\,\omega^2\right)^{\alpha}, \tag{59}$$

where

$$\begin{aligned}\alpha &= -\frac{\gamma}{2(\gamma-1)} - \frac{2-n}{2n(\gamma-1)}\\ &= -\frac{\gamma+1}{2(\gamma-1)} \quad \text{for} \quad n = 1\\ &= -\frac{\gamma}{2(\gamma-1)} \quad \text{when} \quad n = 2.\end{aligned}$$

Table II gives the values of $(-a_1/r_1\lambda_0)$ $(\gamma = 1\cdot4)$ for various values of ω which in term can be evaluated *versus* γ from (57).

TABLE II

$(\gamma = 1\cdot4)$

ω	1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4	2·4495
$-a_1/r_1\lambda_0$ $n=1$	zero	0·014	0·061	0·157	0·293	0·668	2·633	226	∞
$n=2$	zero	0·006	0·025	0·045	0·079	0·139	0·297	2·807	∞

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APPENDIX

Let dS_o denote a differential area on the wave-front $\Sigma(t)$ at $t = 0$. According to a certain mode of propagation of $\Sigma(t)$, let $x_i = x_i(t)$ be the parametric equations of a typical ray of the bundle passing through dS_o at $t = 0$. If dS denotes the differential area on $\Sigma(t)$ at any time $t > 0$ corresponding to dS_o, the correspondence being effected by the rays, then we define the *expansion ratio* $E(t)$ along the ray by the equation

$$E(t) = \frac{(dS)}{(dS_o)}. \tag{A1}$$

Now if dx_i and $d'x_j$ denote the line elements on dS issuing through x_i, then we get

$$n_i dS = \epsilon_{ijk}\, dx_j\, d'x_k, \tag{A2}$$

where ϵ_{ijk} are the usual permutation symbol. If we introduce the material co-ordinates X_i so that

$$x_i = x_i(X_1, X_2, X_3, t), \quad dx_i = \frac{dx_i}{\partial X_j}\, dX_j, \tag{A3}$$

then it readily follows

$$\begin{aligned}\frac{d_r}{dt}(dx_i) &= \frac{\partial}{\partial X_j}\left(\frac{d_r x_i}{dt}\right) dX_j \\ &= V_{i,j}\, dx_j.\end{aligned} \tag{A4}$$

By differentiating (A2) along the rays using (A4) we obtain

$$\frac{d_r}{dt}(n_i dS) = V_{j,j}\, n_i dS - V_{j,i} n_j dS \tag{A5}$$

Dividing (A5) by dS_o (constant quantity) and making use of (A1) we have

$$\frac{d_r}{dt}(n_i E) = E(V_{j,j}\, n_i - V_{j,i}\, n_j). \tag{A6}$$

If we multiply (A6) by n_i and note that $n_i n_i = 1$, we get

$$\frac{d_r}{dt}\log E = V_{j,j} - V_{i,j}\, n_i\, n_j. \tag{A7}$$

Now from (14) and (A7) we finally obtain a useful relation

$$\frac{d_r}{dt}\log(EG) = V_{i,i}. \tag{A8}$$

This relation can also be obtained by applying Gauss's divergence theorem over the volume formed by the tube of rays.[7]

Incidentally we can prove that the expansion ratio is inversely proportional to the Gaussian curvature of the wave-front. For this let us consider a unit sphere with origin at its centre and radii parallel to the normals to $\Sigma(t)$. We denote the differential area, corresponding to dS, on this sphere by dS^+, which is known as the spherical image of dS.

Then it follows that

$$n_i\, dS^+ = E_{ijk}\, dn_j\, d'n_k, \tag{A9}$$

$$\left.\begin{aligned} dn_i &= -K_1 dx_i \\ d'n_j &= -K_2 d'x_j \end{aligned}\right\} \tag{A10}$$

where K_1 and K_2 are principal curvatures of the wave-front $\Sigma(t)$. To obtain (A10) we have taken the Gaussian co-ordinates as lines of curvatures and used the well-known Weingarten formulae (30). Substituting (A10) in (A9) and then using (A2) we get

$$dS^+ = K\,dS, \quad K = K_1 K_2, \tag{A11}$$

where K is the known as Gaussian curvature of the wave-front. Dividing (A11) by dS_o we finally arrive at the relation

$$E^+ = KE, \quad E^+ = (dS^+)/(dS_o). \tag{A12}$$

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When the rays are straight lines, the spherical images of the elementary areas of the wave-fronts at successive positions are the same. Hence from (A12) we conclude that the expansion ratio is inversely proportional to the Gaussian curvature of the wave-front.

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